HETEROBIMETALLIC COMPLEXES OF THE PLATINUM GROUP METALS

by

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Ph.D. Thesis

University of Edinburgh

1987

To my Mother and Father

ACKNOWLEDGEMENTS

I am indebted to my supervisor the late Dr. T.A. Stephenson for his encouragement to study for a Ph.D. and for all his help, guidance and enthusiasm in the first two exciting years. My sincere thanks go to Dr. M. Schroder for his encouragement and helpful comments on the draft manuscript and to Dr. A.J. Blake for the X-ray structure determinations which appear in Chapters 2, 4 and 5. I would also like to thank Dr. G.A. Heath for his comments on Chapter 2, Mr. J.R.A. Millar and others for recording n.m.r. spectra and the technical staff of the Analytical and Mass Spectroscopy services of the University of Edinburgh.

I am grateful to the S.E.R.C. and the I.C.I. Educational Trust for financial support and to the University of Edinburgh for use of the laboratory facilities.

Finally, I would like to thank Mrs. C.G. Ranken for typing this thesis.

ABSTRACT

Chapter 1: The relevance of locating metal centres in close proximity is discussed. Some methods for the preparation of heterobimetallic complexes are reviewed. Consideration is given to mononuclear complexes which contain oxy, thio or phosphorus ligands with the ability to capture a second metal fragment.

Chapter 2: A brief survey of the chemistry of $[CODMCl]_2$ (M=Rh,Ir) is given. Heterobimetallic complexes of the type $[CODM(XPPh_2)(YPPh_2)Pt(S_2CNR_2)]$ (M=Rh,Ir; X,Y=S,S; S,O; O,O) are prepared and the substitution of the cyclo-octadiene ligand by CO and phosphine ligands described. The X-ray crystal structures of $[CODRh(SPPh_2)_2Pt(S_2CNEt_2)]$ and $[CODIr(SPPh_2)_2Pt(S_2CN^iPr_2)]$ are reported. The reaction of $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ with $[CODMCl]_2$ to give the trimetallic salts $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2MCOD\}Y$ ($Y=BPh_4^-$, PF_6^-) is discussed.

Chapter 3: A brief survey of the chemistry of $[(arene)MCl_2]_2$ (M=Ru,Os) is given. The heterobimetallic complexes $[(arene)MCl(SPPh_2)_2Pt(S_2CNR_2)]$ (M=Ru, arene = C_6H_6, p-cymene, C_6Me_6; M=Os, arene = p-cymene) are prepared and the substitution of the terminal-chloride ligand by CO, phosphine, acetylene and dithio ligands described. The mixed-, asymmetric- and singly-bridged heterobimetallic complexes $[(p\text{-cym})MCl(SPPh_2)(OPPh_2)Pt(S_2CNR_2)]$ (M=Ru,Os), $[(p\text{-cym})RuCl(EPPh_2)(PPh_2)Pt(S_2CNR_2)]$ (E=S,Se) and

$[(p\text{-cym})MCl_2(SPPh_2)(MeOPPh_2)Pt(S_2CNR_2)]$ (M=Ru,Os) are reported. Heterobimetallic complexes incorporating the $M(C_5Me_5)^{2+}$ (M=Rh,Ir) fragment are also presented.

Chapter 4: The preparation of the mononuclear complexes $[(C_5Me_5)M(S_2CNEt_2)(\text{diphosphine-P})]BPh_4$ (M=Rh, diphosphine = dppm, dppe, dppp, dmpe; M=Ir, diphosphine = dppm, dppe) is described. The X-ray crystal structure of $[(C_5Me_5)Rh(S_2CNEt_2)(\text{dppm-P})]^+$, which shows the diphosphine ligand bound in a monodentate fashion is presented. Treatment of $[(\text{arene})M'Cl_2]_2$ (M'=Ru, arene=C_6H_6, p-cym, C_6Me_6; M=Os arene = p-cymene) with $[(C_5Me_5)M(S_2CNR_2)(\text{diphosphine-P})]BPh_4$ in a 1:2 molar ratio produces the heterobimetallics $[(C_5Me_5)M(S_2CNR_2)(\mu\text{-diphosphine})M'Cl_2(\text{arene})]BPh_4$ (not all combinations). The X-ray crystal structure of $[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(C_6Me_6)]^+$ is reported. The complexes $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RuCl(PPhMe_2)(p\text{-cym})]^{2+}$, $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-diphosphine})IrCl(COD)]^+$ and $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})Ru(p\text{-cym})(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]^{2+}$ are discussed.

Chapter 5: The preparation of mononuclear complexes of the type $[(\text{arene})Ru(PR_3)(\text{diphosphine-P})Cl]Y$ (diphosphine = dppm, dppe, dppp; PR_3=PPh_3, $PPhEt_2$, $PPhMe_2$, $P(OMe)_3$; arene = C_6H_6, p-cymene; not all combinations) containing terminal chloride and dangling diphosphine ligands is described. The homobimetallic complexes $\{[(\text{arene})MCl(PPhMe_2)]_2(\mu\text{-diphosphine})\}[PF_6]_2$ (M=Ru,Os; arene = C_6H_6, p-cymene; diphosphine = dppe, dppp; not all combinations) are prepared and the X-ray crystal

structure of $\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppe})\}^{2+}$ reported. Treatment of $[(arene)M'Cl_2]_2$ (M'=Ru,Os) or $[CODIrCl]_2$ with $[(arene)Ru(PR_3)(diphosphine\text{-}P)Cl]Y$ in a 1:2 molar ratio produces heterobimetallics of the type $[(arene)RuCl(PR_3)(\mu\text{-diphosphine})M'Cl_2(p\text{-cym})]Y$ and $[(arene)RuCl(PR_3)(\mu\text{-diphosphine})IrCl(COD)]Y$ (diphosphine=dppm,dppe) respectively. The reaction of $[(arene)M'Cl_2]_2$ with diphosphines is discussed and the preparation of the unusual complex $[(p\text{-cym})Ru(dppe\text{-}P)Cl(\mu\text{-dppe})RuCl_2(p\text{-cym})]BPh_4$ containing a bridging and a dangling dppe ligand described. Finally, some suggestions for future work are given.

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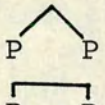
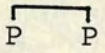
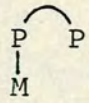
LIST OF ABBREVIATIONS

'oxyring' complex	$L_nMR_2POHOPR_2$
'oxytripod' complex	$L_nM(PR_2O)_3H_2$
1,5-COD	cycloocta-1,5-diene
$acac^-$	acetylacetonate
bipy	bipyridine
1,10-phen	1,10-phenanthroline
py	pyridine
p-cym(ene)	2-methyl-5-isopropylbenzene
dppm	1,1-bis(diphenylphosphino)methane 
dppe	1,2-bis(diphenylphosphino)ethane 
dppp	1,3-bis(diphenylphosphino)propane
dmpe	1,2-bis(dimethylphosphino)ethane
dpae	1,2-bis(diphenylarsino)ethane
	general diphosphine ligand
E	chalcogenide atom O,S,Se
X	halogen ligand Cl,Br,I
Y	general anionic counterion
R	general alkyl group
L	general monodentate ligand
	general bidentate ligand
dangling diphosphine	monodentate pendant diphosphine ligand 
NBD	norbornadiene
c ht	cycloheptatriene
dba	dibenzylideneacetone
pyz	pyrazine

CONTENTS

CHAPTER 1

A SURVEY OF SYNTHETIC METHODS USED FOR THE PREPARATION OF HETEROMETALLIC COMPLEXES

1.1 INTRODUCTION

In the last ten years considerable attention has focussed on the preparation of complexes containing more than one metal centre. It is anticipated that active metal sites in close proximity will reveal new, distinctive reactivity only accessible through the participation, either electronic and/or steric, of both metals[1]. The coordination of a substrate by two or several metals can generate interesting ligand coordination modes and may allow simple conversion through enhanced-ligand activation[2]. In addition the existence of intimate metal centres may facilitate multielectron redox processes which would be unachievable with a single metal centre[3]. Another possibility is that of a dual- or multi-functional catalyst in which each metal component would perform a designated role to realise an overall process[4].

In bimetallic complexes there is increased scope for modifying the steric and electronic environment of the metals, giving an increase in versatility over mono-metallic systems. This may be achieved through ligand alteration or through locating unlike metals in the structure. It is increasingly more obvious that to exploit fully the potential of bimetallic complexes, rational and systematic methods for their preparation are required. On this theme, the work presented here formulates methods for the controlled construction of mainly heterobimetallic complexes containing the Platinum group metals. The

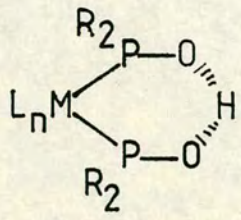
approach used was to identify or synthesise a mono-metallic complex that contained a ligand or ligands with a suitable donor atom to accommodate a second metal fragment. Chapters 2 and 3 develop this concept with some platinum complexes containing phosphine chalcogenide ligands prepared earlier by Anderson[5]. The work in Chapters 4 and 5 utilises new rhodium, iridium and ruthenium diphosphine complexes prepared as part of this research. Some background chemistry to this work is now presented.

1.2 THE USE OF TRANSITION METAL COMPLEXES OF SECONDARY PHOSPHINE CHALCOGENIDES AND RELATED COMPLEXES IN THE PREPARATION OF HETEROBIMETALLIC COMPOUNDS

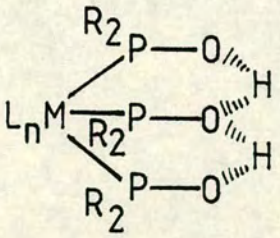
Two comprehensive reviews have been published on the coordination chemistry of the secondary phosphine chalcogenides $R_2P(E)H$ (E=O,S,Se; R = alky, aryl)[6,7] and several recent works also review the subject[5,8,9]. The following discussion will therefore only concern areas relevant to this work.

1.2.1 DIALKYL PHOSPHINE OXIDE TRANSITION METAL COMPLEXES

Over the past twenty years, a considerable number of transition metal complexes incorporating the six-membered 'oxyring' moiety (1) have been described[7].

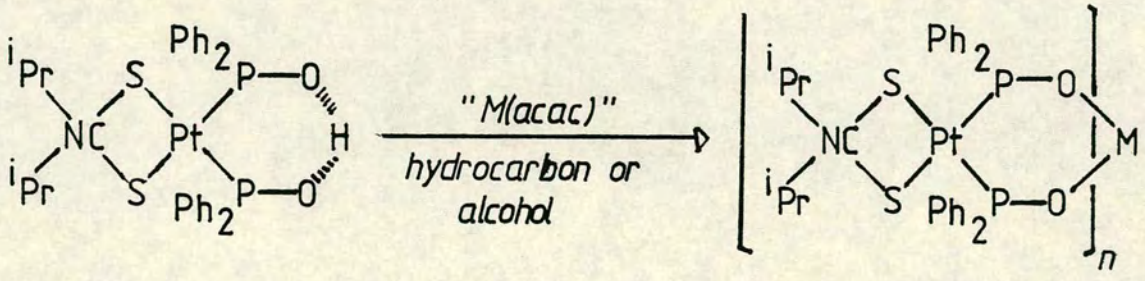


(1)



(4)

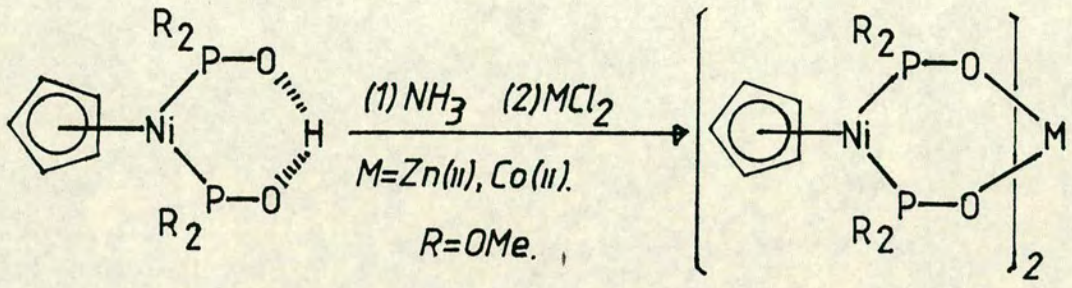
Several of these complexes, such as $[Pd(S_2PMe_2)(Ph_2PO)_2H]$[10], $[Pd(SCN)(Ph_2PO)_2H]_2$[11], $AsPh_4[RhCl_5(Ph_2PO)_4H_2]$[12], $[Os(C_6H_6)I(P(OMe)_2O)_2H]$[13] and $[NEt_4][Mo(CO)_4(Ph_2PO)_2H]$[14] have been characterised crystallographically. Complexes containing the 'oxyring' moiety are frequently compared with simple acetylacetonate ($acac^-$) ligands since the 'oxyring' complexes function as bidentate O,O-donor ligands. On treatment of a first row transition metal chloride, acetate, or acetylacetonate, a range of heterometallic compounds can be produced (Equations 1-3).



[15] ---------- [1]

n=2; M= VO(IV), Co(II), Cu(II), Ni(II).

n=3; M=Mn(III).



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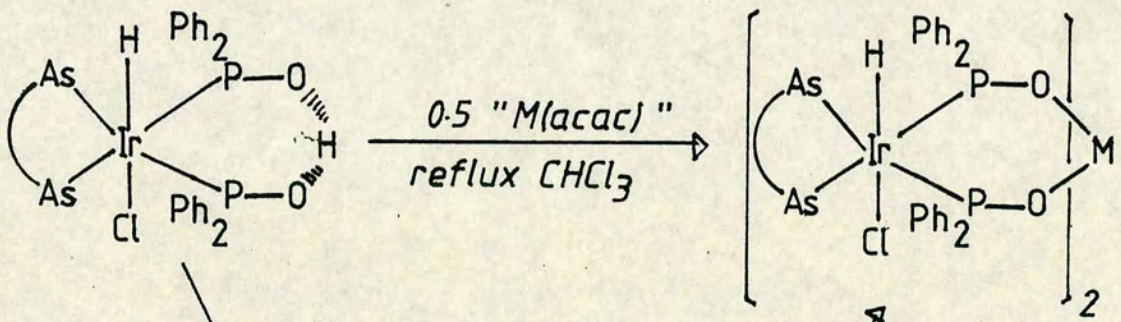

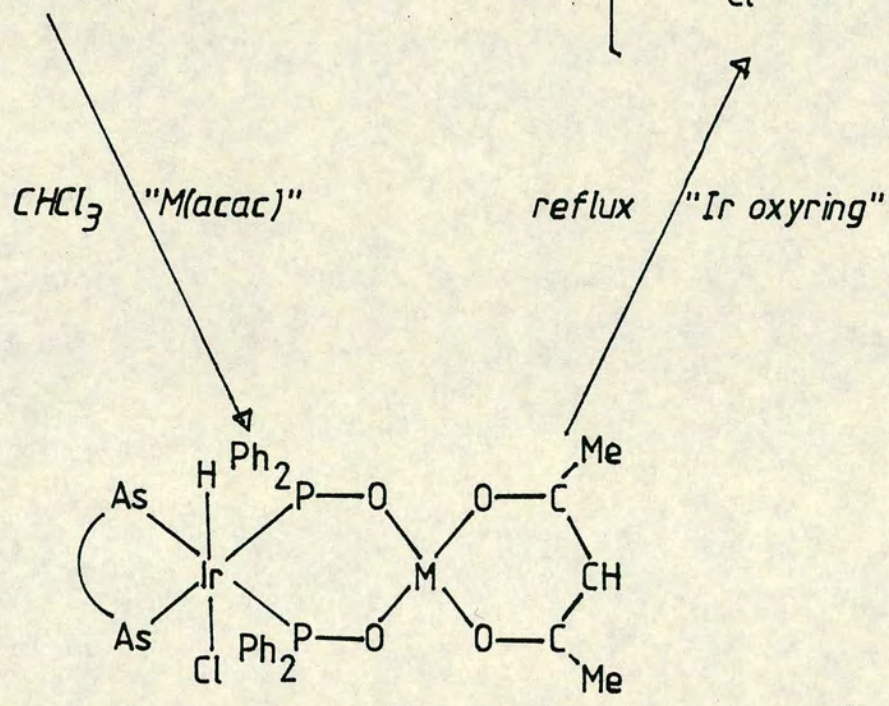

M=VO(IV), Co(II).

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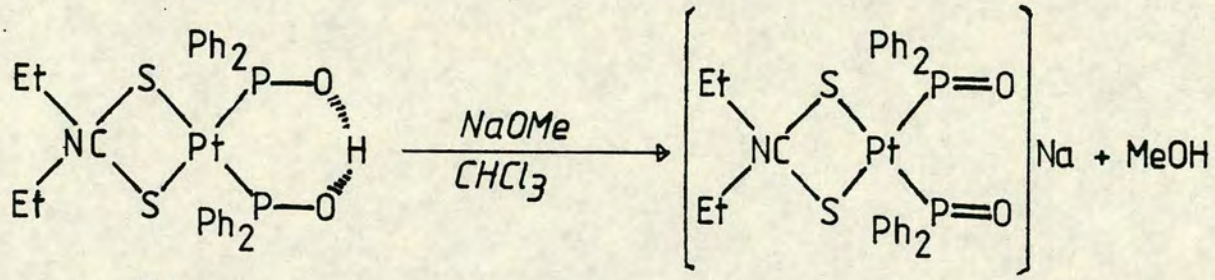
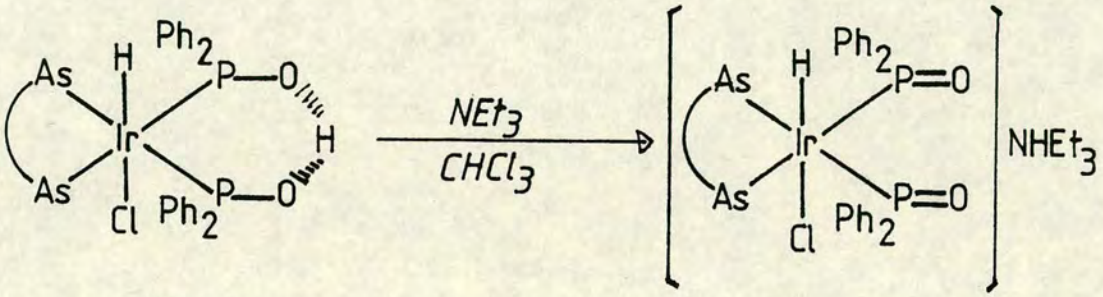
---------[3]

Mixed-metal complexes of the type $[PtCl(PR_3)(P(OMe)_2O)_2]_nM$ (n=2; M=Cu(II),UO_2(VI), Co(II); n=4; M=Th(IV)) and $\{[Pt(\overset{\frown}{L\ L})(P(OMe)_2O)_2]_2M\}(ClO_4)_2$ ($\overset{\frown}{L\ L}$ = dppe, M=Cu(II),Co(II),Ni(II),Zn(II)) have also been reported[18]. To date, the coordination chemistry of 'oxyring' ligands has been confined to so-called 'hard' (class a) transition metal centres which is consistent with the 'hard' (class a) nature of the oxygen donor atoms. In Chapters 2 and 3, $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ (2) and $[IrHCl(dpae)(Ph_2PO)_2H]$ (3) are used to extend the range of metals, that can be coordinated by an 'oxyring' donor arrangement, to include the 'soft' (class b) Platinum metal centres Rh(I),Rh(III),Ir(I) and Ru(II). However, this was only achieved after removal of the acidic proton, to generate <u>in situ</u> the more reactive anionic 'oxyring' complex [Equations 4 and 5], prior to reaction with the Platinum metal substrate.



(2)

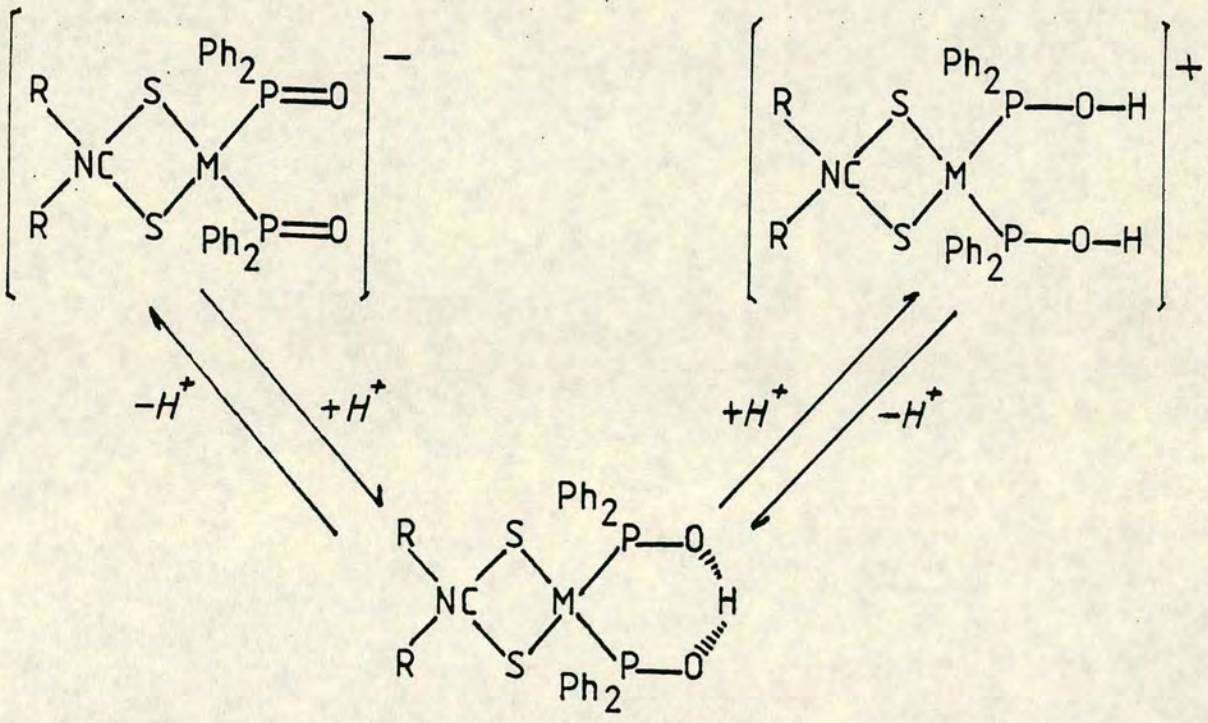
--------[4]



(3)

--------[5]

Deprotonation reactions and replacement of the ring proton by groups such as 'BF_2^+' (from BF_3) and '$SiMe_3^+$' (from $SiClMe_3$) appear characteristic reactions of 'oxyring' compounds. A detailed study of the deprotonation/protonation reactions of the related compounds $[M(S_2CNR_2)(Ph_2PO)_2H]$ (M=Pt(2), M=Pd, R=Et; M=Ni, [19]; R=^{i}Pr) was made during this work[20]. $^{31}P-\{^1H\}$ n.m.r. evidence suggests that an equilibrium exists between the neutral parent complex and its anion and cation in solution [Equation 6]. The position of equilibrium can be altered by addition of either base (NaOMe,BuLi) or acid (HBF_4) and the phosphorus chemical shift (δP) is very sensitive to the change [Table 1]. Interestingly, for the compounds $[M(S_2CNR_2)(Ph_2PO)_2H]$ a plot of δP against equilibrium state produces a straight line graph [Graph 1]. This, in principle, can be used to determine the position of equilibrium from a measurement of δP.

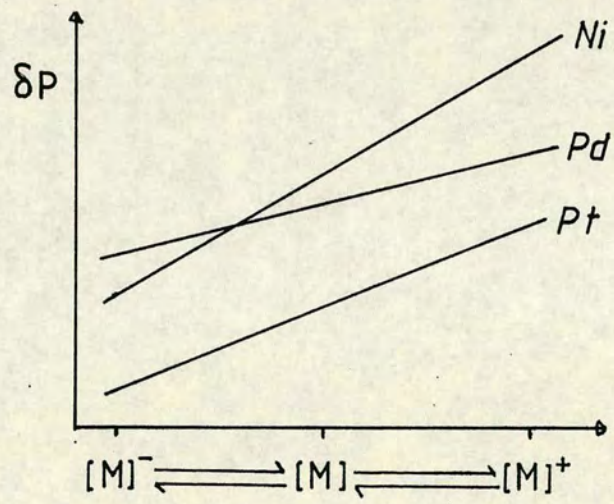


(2)

---------[6]

		CHEMICAL SHIFT δP/ppm (a)			
M	R	[OXYRING]$^-$ (b)	OXYRING	[OXYRING]$^+$ (c)	"BF_2^+" CAPPED
Ni	^{i}Pr	64.8 (d)	96.5	114.6 (d)	108.4
Pd	Et	71.0	84.3	99.0	-
Pt	Et	45.0	62.5	78.6	72.4

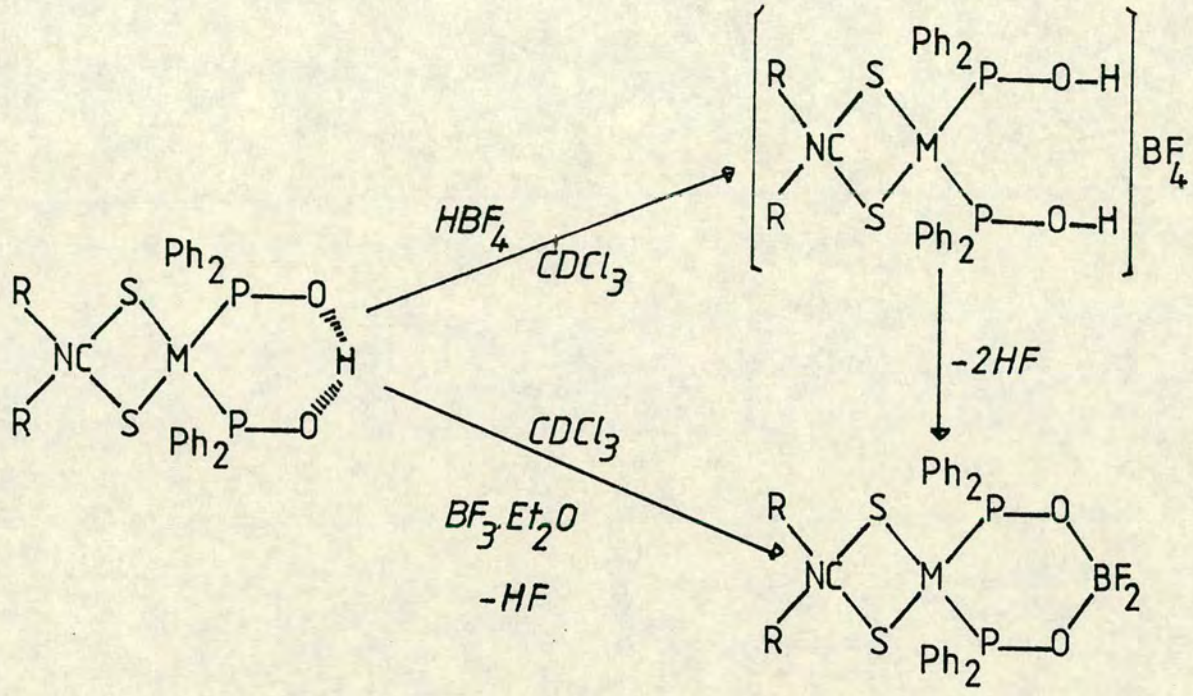
Table 1. (a) Samples run in $CDCl_3$ at R.T. (b) Formed by addition of large excess of LiBu to neutral complex. (c) Formed by addition of large excess of HBF_4 to neutral complex. (d) Some decomposition suspected.



Graph 1. Graph of δP against equilibrium state for $[M(S_2CNR_2)(Ph_2PO)_2H]$ (M = Pt, Pd, Ni)

The equilibrium [Equation 6] also appears to be influenced by temperature and at low temperature is shifted in favour of the 'oxyring' anion. After protonation of $[M(S_2CNR_2)(Ph_2PO)_2H]$ with HBF_4 to give $[M(S_2CNR_2)(Ph_2POH)_2]$-BF_4 a loss of HF can occur to yield the 'BF_2^+' capped

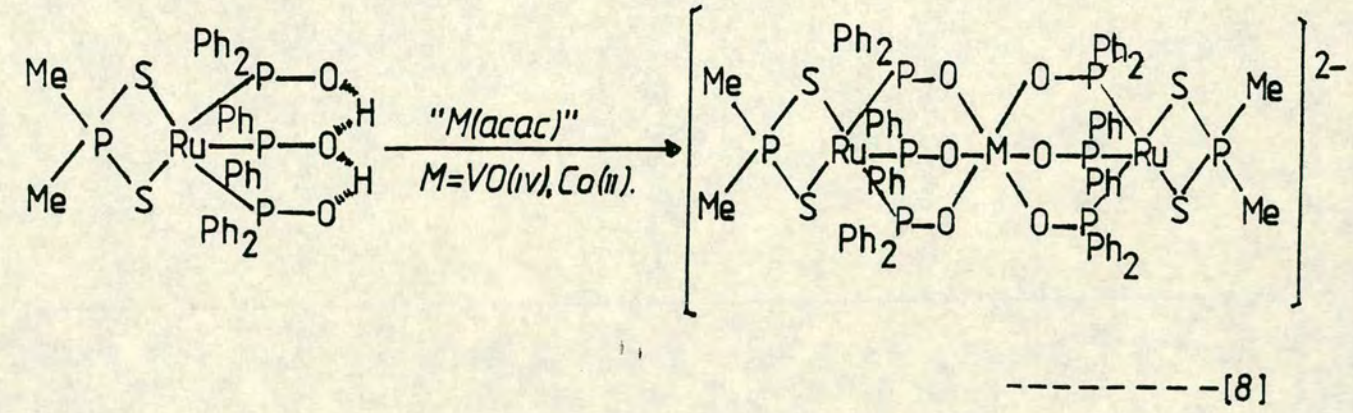
species $[M(S_2CNR_2)(Ph_2PO)_2BF_2]$ [Equation 7].



--------[7]

This type of rearrangement reaction has been reported for a number of 'oxyring' complexes including (3)[21] and $[(C_5H_5)Ni(P(OMe)_2O)_2H]$[16].

As well as compounds containing the 'oxyring' moiety (1), a number have been prepared which incorporate an 'oxytripod' (4) ligand arrangement. Some examples include $Na[Co(C_5H_5)(PR_2O)_3]$ (R = OMe[22], OEt[178]) $[Rh(NO_3)Cl(PPh_2O)_3H_2]$;[9] $[(Ph_2POMe)_2(Ph_2POH)RuCl_3Ru(Ph_2PO)_3H_2]$[23] $[Ru(S_2PMe_2)(Ph_2PO)_3H_2]$[24] and $Na[Rh(C_5Me_5)(P(OMe)_2O)_3]$[25]. Several of these function as tridentate oxygen ligands for various 1st row transition metal ions [Equations 8 and 9] and in the case of $Na[M(C_5R_5)(PR_2O)_3]$ for the Platinum metals Ru(II) and Rh(III) [Equation 9].



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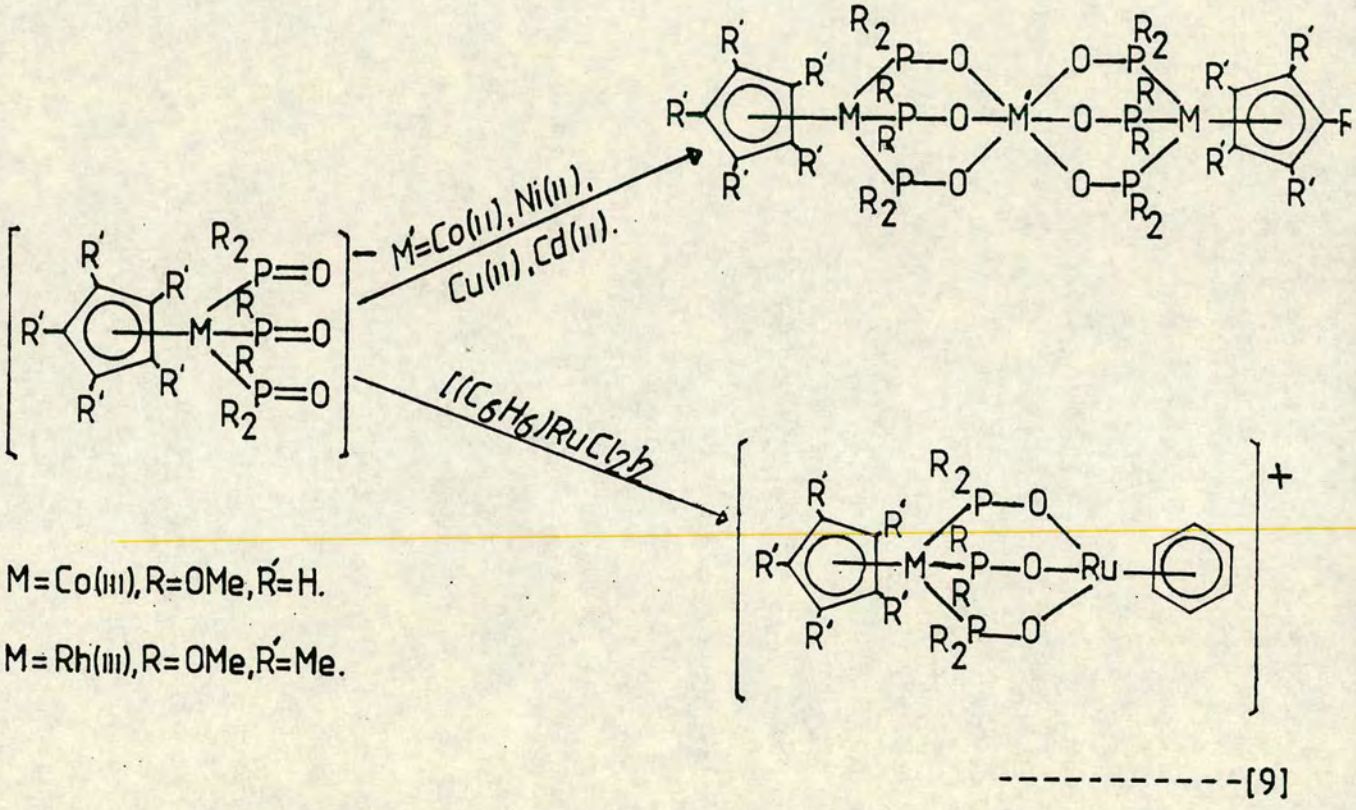
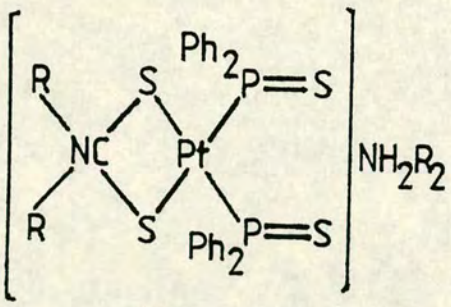


----------[9]

1.2.2 DIALKYLPHOSPHINE SULPHIDE TRANSITION METAL COMPLEXES

Work on the coordination chemistry of secondary phosphine sulphides and selenides has received less attention. Only recently have thio analogues of (1) been prepared. Anderson[5] investigated the reactions of the

diphenyl phosphine chalcogenide ligands $Ph_2P(E)H$ (E = O,S,Se) with a number of square planar platinum(II) and palladium(II) complexes containing mono-anionic bidentate ligands $[M(\widehat{S\ S})_2]$ ($\widehat{S\ S}^-$ = $S_2CNR_2^-$, $S_2PR_2^-$, S_2CPh^-). It was hoped that displacement of a single ligand would create two free, mutually-cis, coordination sites allowing formation of complexes containing the '$\overline{MPh_2PEHEP}Ph_2$' moiety. The most successful reaction was that of $Ph_2P(E)H$ with $Pt(S_2CNR_2)_2$ which for E=O and E=Se gives the single reaction products $[Pt(S_2CNR_2)(Ph_2PO)_2H]$ (2) and $[Pt(S_2CNR_2)(Ph_2PSe)(Ph_2PH)]$ (5). In contrast, for E=S a variety of products are formed depending on the amount of sulphide used, the amount of water present in the reaction mixture and the duration of the reaction. A possible mechanism to account for the formation of the five metal complexes in the reaction of $Ph_2P(S)H$ with $Pt(S_2CNR_2)_2$ has been proposed [Scheme 1][26]. Evidence for the formulations (5-10) are based on elemental analysis, conductivity measurements, and variable-temperature ^1H, $^{31}P-\{^1H\}$, $^{13}C-\{^1H\}$ and $^{195}Pt-\{^1H\}$ n.m.r. studies. In addition X-ray structural analysis confirmed the formations $[NH_2Et_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (6) and $[Pt(S_2CN^iPr_2)(Ph_2PS)]_2$ (8). Preliminary investigation by Anderson revealed the dithio(6)- and monothio(7)-complexes function as bidentate S,S-(pseudo sacsac) and S,O-(pseudo sacac) chelate ligands for a range of metals.



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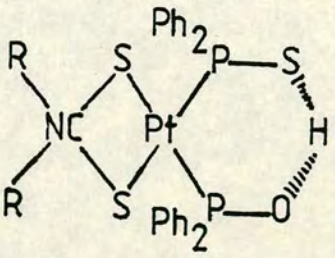
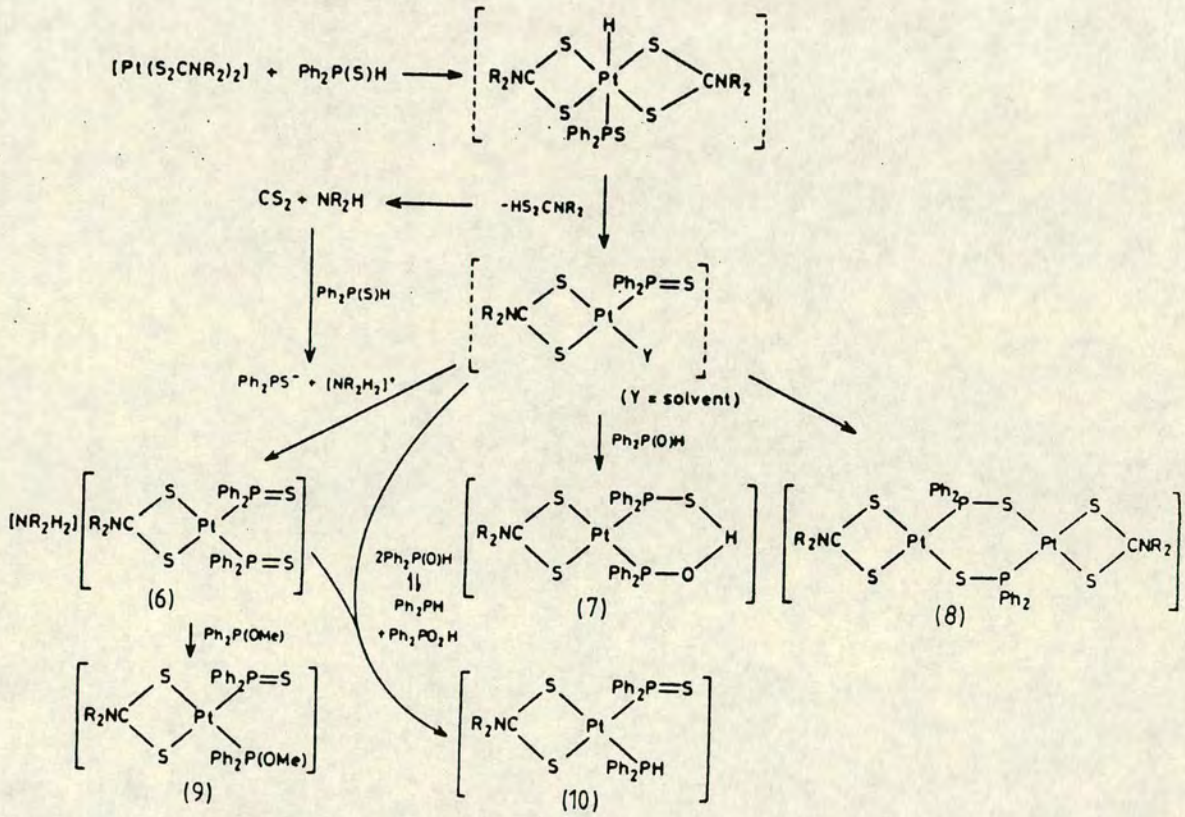


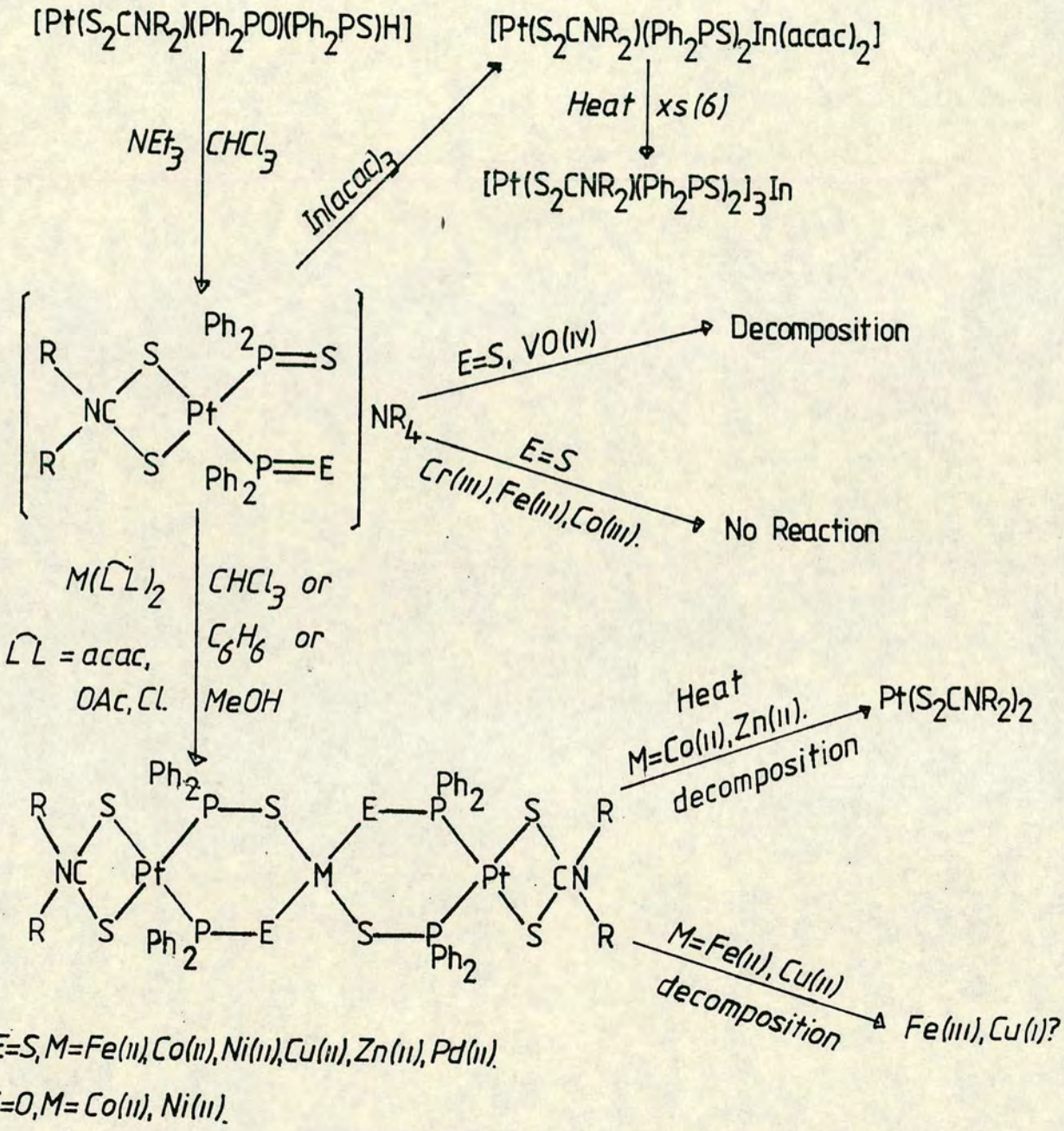
(7)

In contrast to the 'oxyring' species (1), and in particular (2), reaction of (6) with a range of first row transition metal acetylacetonate, acetate or halide compounds was not totally successful [Scheme 2]. The failure of (6) to coordinate the early transition metal ions such as VO(IV) and Cr(III) is most probably due to the 'soft' (class b) nature of the sulphur chelate. However reaction of (6) with the 'soft' (class b) Platinum metals Pd(II) and Pt(II) proved extremely facile.



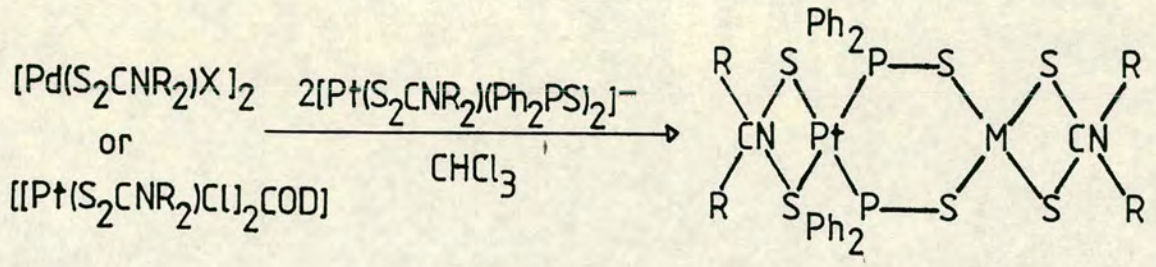
Scheme 1: A mechanism for the reaction of $Pt(S_2CNR_2)_2$ with $Ph_2P(S)H$

Scheme 2: The reaction of $[NR_4][Pt(S_2CNR_2)(Ph_2PS)(Ph_2PE)]$ with various first row transition metal ions.



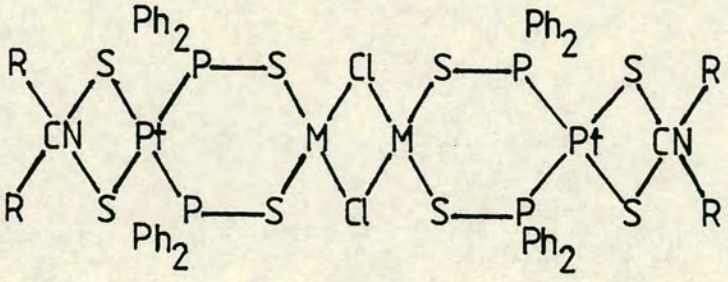
In reactions of (6) with Pt(II) or Pd(II) compounds containing halide or diene bridges, yellow Pt-Pt or orange Pt-Pd bimetallics are formed under mild conditions [Equation 10]. An X-ray structure of

$[Pt(S_2CN^iPr_2)(Ph_2PS)_2Pt(S_2CNEt_2)]$ confirms the bimetallic formulation[5].



----------[10]

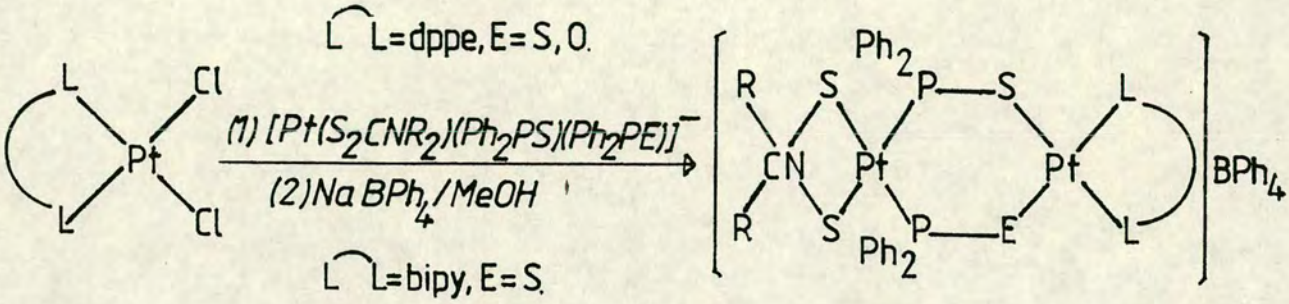
The reaction of (6) with $PdCl_2$(1,5-COD), trans-$PdCl_2(PhCN)_2$ or $PdCl_4^{2-}$ under a variety of room temperature conditions is suspected to give the same product (11a) although the insolubility of the product does not exclude formation of polymeric species of the type $\{PdCl[Pt(S_2CNR_2)(Ph_2PS)_2]\}_n$. With $PtCl_4^{2-}$ or $PtCl_2$(1,5-COD) an analogous product (11b) is eventually formed. However in the reaction of (6) with $PtCl_2$(1,5-COD), the cyclooctadiene-bridged intermediate $[PtCl\{Pt(S_2CNR_2)(Ph_2PS)_2\}]_2$-(1,5-COD) has been identified and isolated.



(11a) M=Pd
(11b) M=Pt

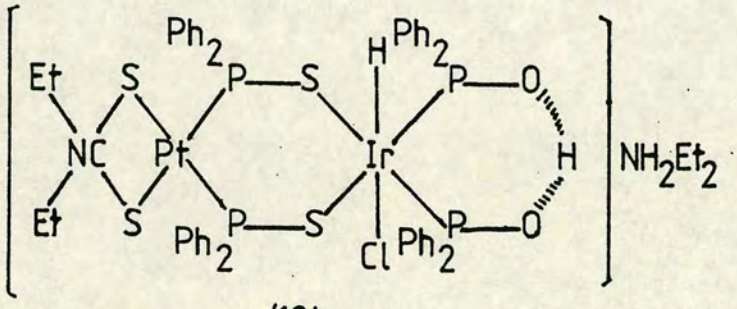
Cationic homobimetallic complexes of the type $[Pt(S_2CNR_2)(Ph_2PS)_2Pt(\overset{\frown}{L\ L})]BPh_4$ ($\overset{\frown}{L\ L}$ = dppe, bipy) can

also be isolated from rapid room temperature reactions [Equation 11].



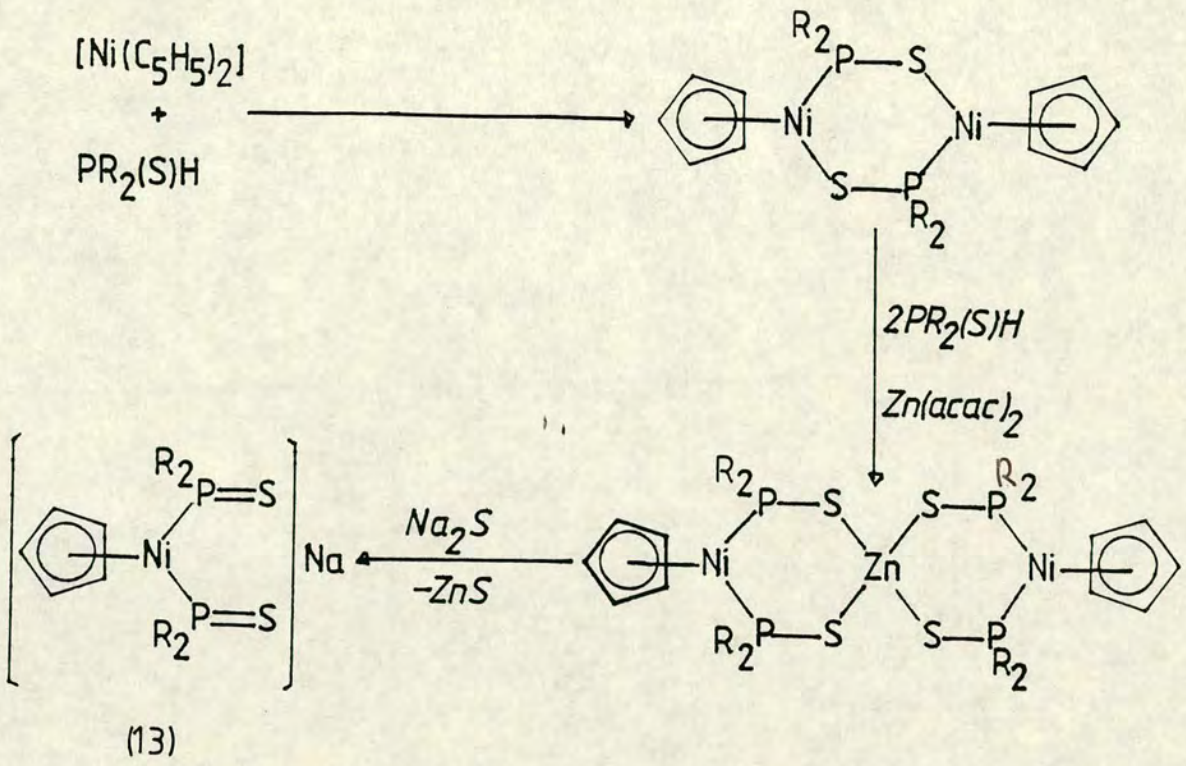
--------[11]

Finally for (6), if mixed with an equimolar quantity of $[IrHCl(1,5\text{-COD})(Ph_2PO)_2H]$ in $CHCl_3$ at room temperature, the labile 1,5-COD ligand is substituted to give the unusual heterobimetallic complex (12), which retains an 'oxyring'-ligand arrangement with the potential for coordinating a further metal[27].



(12)

The palladium analogue of (6), $[NH_2R_2][Pd(S_2CNR_2)(Ph_2PS)_2]$, can be prepared from $Pd(S_2CNR_2)_2$ and $Ph_2P(S)H$[5]. The only other reported example of a thio analogue of (1) appears to be the anionic-cyclopentadienyl nickel complex $Na[C_5H_5Ni(PR_2S)_2]$ (13)(R=OCH_3, R=Me) prepared by Klaui and co-workers by an indirect route from Nickelocene and $PR_2(S)H$ involving a Zn^{2+} template reaction[28,29]. (Scheme 3)

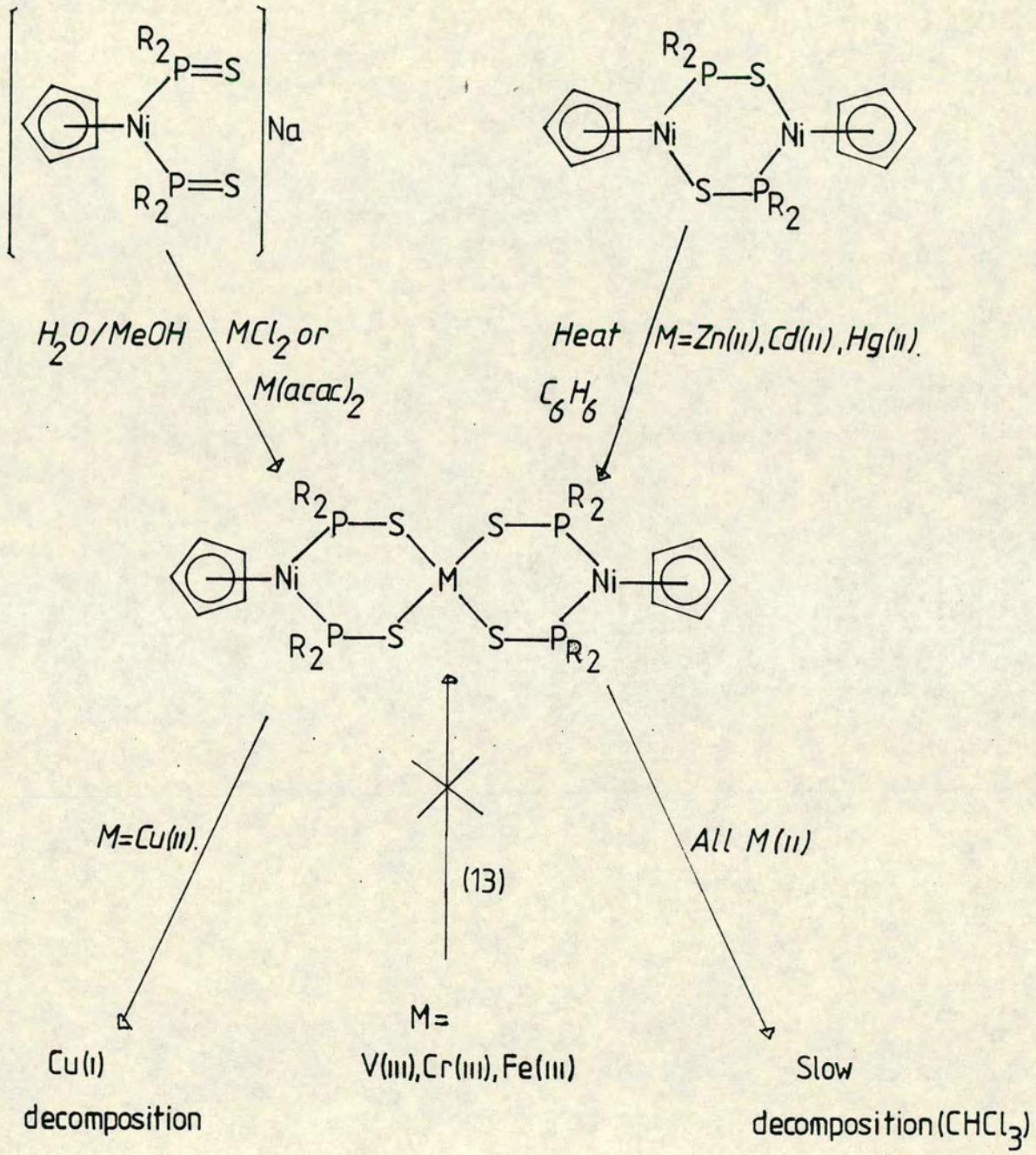


Scheme 3. Formation of $Na[Ni(C_5H_5)(PR_2S)_2]$ (R=OCH_3, Me)

An X-ray structural analysis has confirmed the formulation for the intermediate complex $[C_5H_5Ni(PMe_2S)]_2$[30]. The complex (13) functions as a bidentate S,S-chelate ligand and like (6) reaction with various first row Transition metal ions brings only partial success[31]. (Scheme 4)

The coordination chemistry of the S,O-chelate complex $[Pt(S_2CNR_2)(Ph_2PO)(Ph_2PS)H]$ (7) is limited to that described in Scheme 2 and Equation [11] and the potential coordination chemistry of (5) and (8-10) unexplored.

In Chapters 2 and 3 the reactivity of the platinum species (2) and (5-10) is investigated or developed. All are shown to be useful synthetic precursors for the synthesis of novel heterobimetallic complexes with the chalcogenide atom acting as a site for an additional metal fragment.

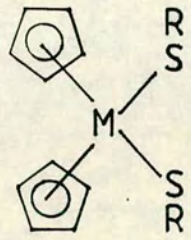


M=Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II).

Scheme 4: The reaction of $Na[C_5H_5Ni(PR_2S)_2]$ with various first row transition metal ions.

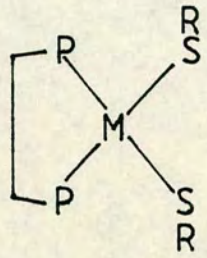
1.3 OTHER BIDENTATE S,S-DONOR METAL COMPLEXES

Thiol complexes of the type $[(C_5H_5)_2M(SR)_2]$ (14) and $[(dppe\text{-}P,P)M(SR)_2]$ (17) have successfully been used to synthesise a range of heterometallic systems [Equation 12].



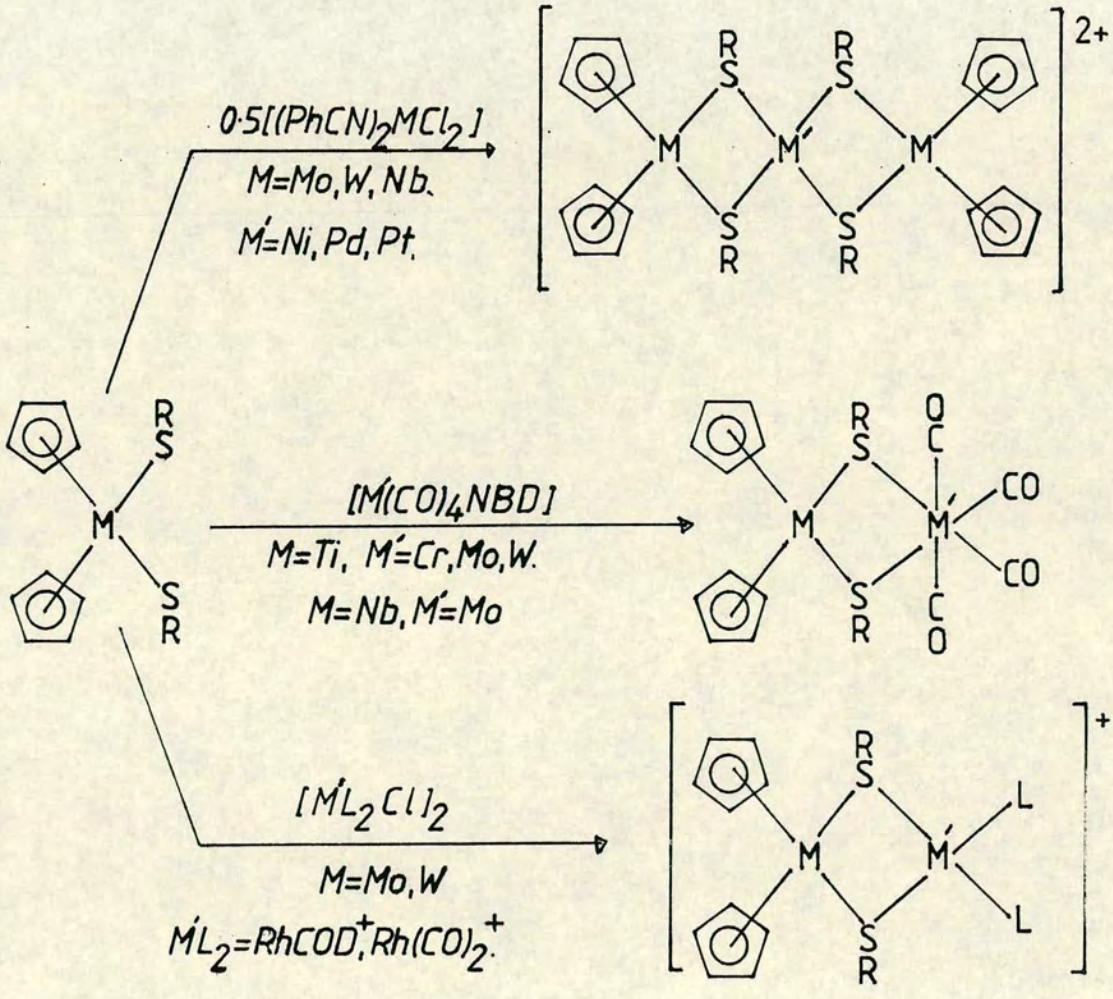
(14)

M	R	Ref.
Ti	Me,Ph	32
Mo,W	Me	33
Nb	Me,Ph	34



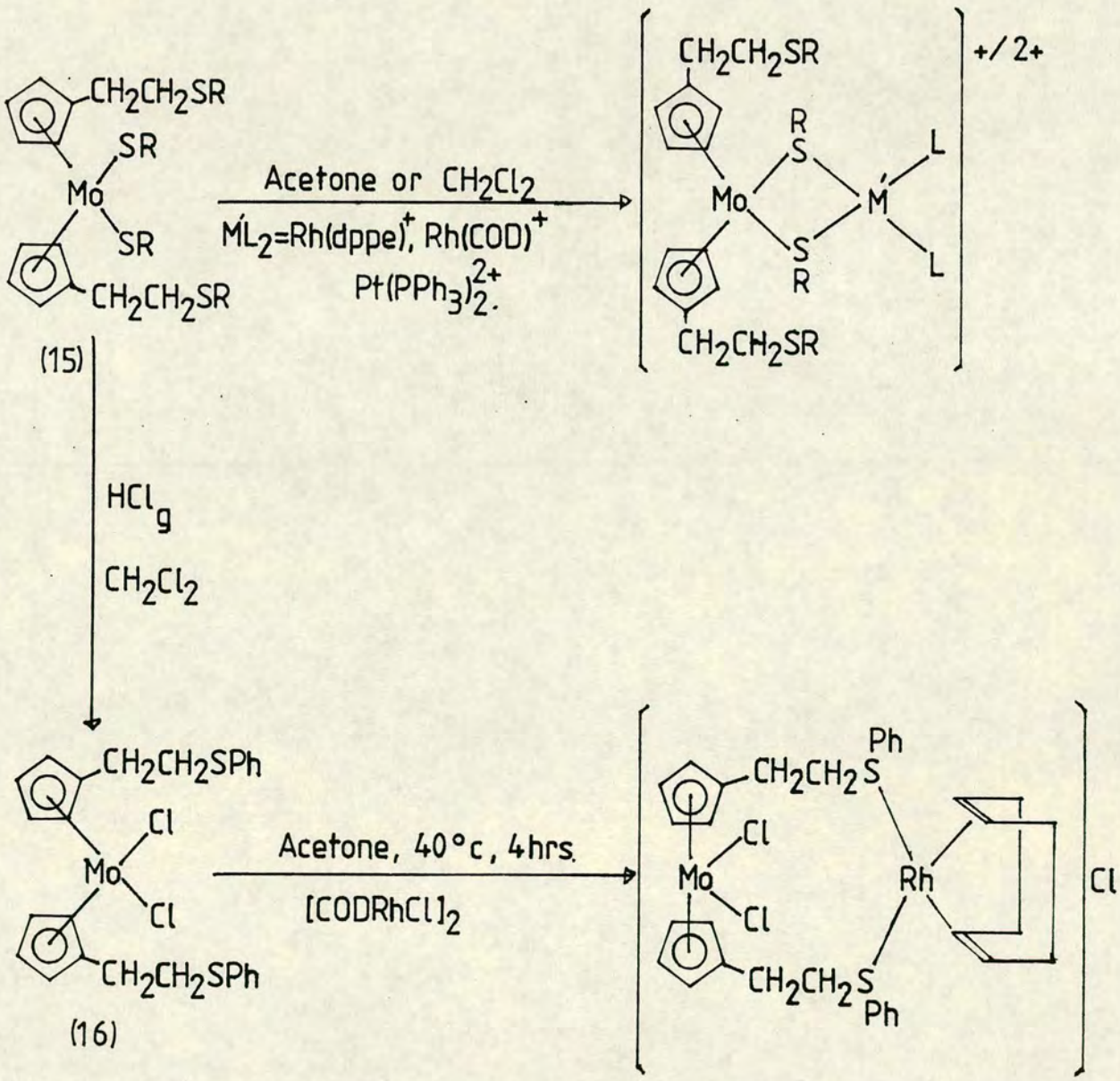
(17)

M	R	Ref.
Pd,Pt	Me,Ph	35



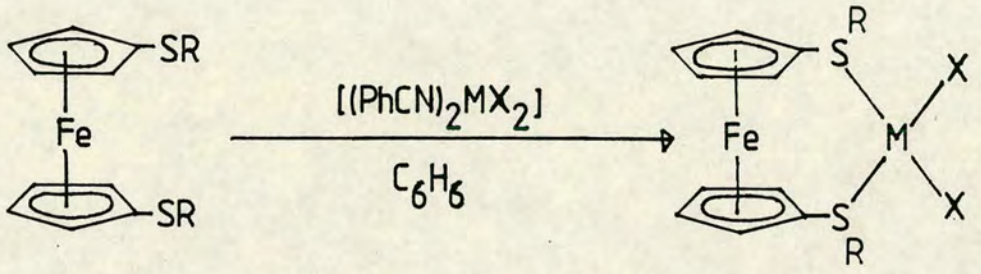
---------- [12]

The related complex $[Mo(C_5H_4(CH_2)_2SR)_2(SR)_2]$ (15) is a potential tetradentate sulphur ligand. Treatment of (15, R = Pr^n) with $[(dppe)Rh(acetone)_2]BF_4$, $[(COD)RhCl]_2$ or $[(PPh_3)_2PtCl_2]$ however gives bidentate coordination through the $M(SR)_2$ group as for (14). The complex $[Mo(C_5H_4(CH_2)_2SPh)_2Cl_2]$ (16) is formed on reaction of (15, R = Ph) with HCl gas. The sulphur atoms of the substituted cyclopentadienyl ring of (16) are utilised in forming $[Mo(C_5H_4(CH_2)_2\text{-}\mu\text{-}SPh)_2\ Cl_2Rh(COD)]Cl$ in reaction with $[(COD)RhCl]_2$ [36,37] [Scheme 5].



Scheme 5: Reactions of $[Mo(C_5H_4(CH_2)_2SR)_2(SR)_2]$ (15)

Similarly the ferrocene derivative $[Fe(C_5H_4SR)_2]$ (R=Me, ^1Pr, ^1Bu, Ph, CH_2Ph) acts as a bidentate S,S-donor ligand in reaction with $[(PhCN)_2MX_2]$ to give products of the type $[Fe(C_5H_4-\mu-SR)_2MX_2]$ (M=Pt, Pd, X=Cl, Br) [Equation 13]. An X-ray crystal structure determination has been carried out for $[Fe(C_5H_4-\mu-S^1Bu)_2PdCl_2]$[38].



--------[13]

The compound $[Pt_2(\mu-S)_2(PPh_3)_4]$ (64) is a useful precursor for the synthesis of a range of heterometallic compounds. The lone pairs on the sulphido-bridges are of sufficient basicity to coordinate the metal ions Ag(I), Hg(II), Pd(II) and Ni(II) forming 'aggregates' of up to six metals[39,40,180]. Finally in this section, the complex $[Rh_2(\mu_2-C_7H_4NS_2)_2(COD)_2]$ coordinates <u>via</u> the thiolate sulphur atoms the metal fragments $AgPPh_3^+$, CuCl, AuCl and $Rh(COD)^+$ to give trinuclear aggregates[41].

1.4 THE USE OF METAL COMPLEXES CONTAINING DIPHOSPHINE AND RELATED LIGANDS FOR THE PREPARATION OF HETEROBIMETALLIC COMPOUNDS

Bis(diphenylphosphino)methane (dppm) is probably the

most versatile and potentially the most useful of the large family of diphosphine ligands. Its ability to function as a bridging ligand is considerable and a vast chemistry has been developed for homobimetallic complexes of the general types shown in Figure 1, where M is usually Pd, Pt, Rh or Ir but can be Mo, Mn, Re, Cu, Ag or Au[42,43].

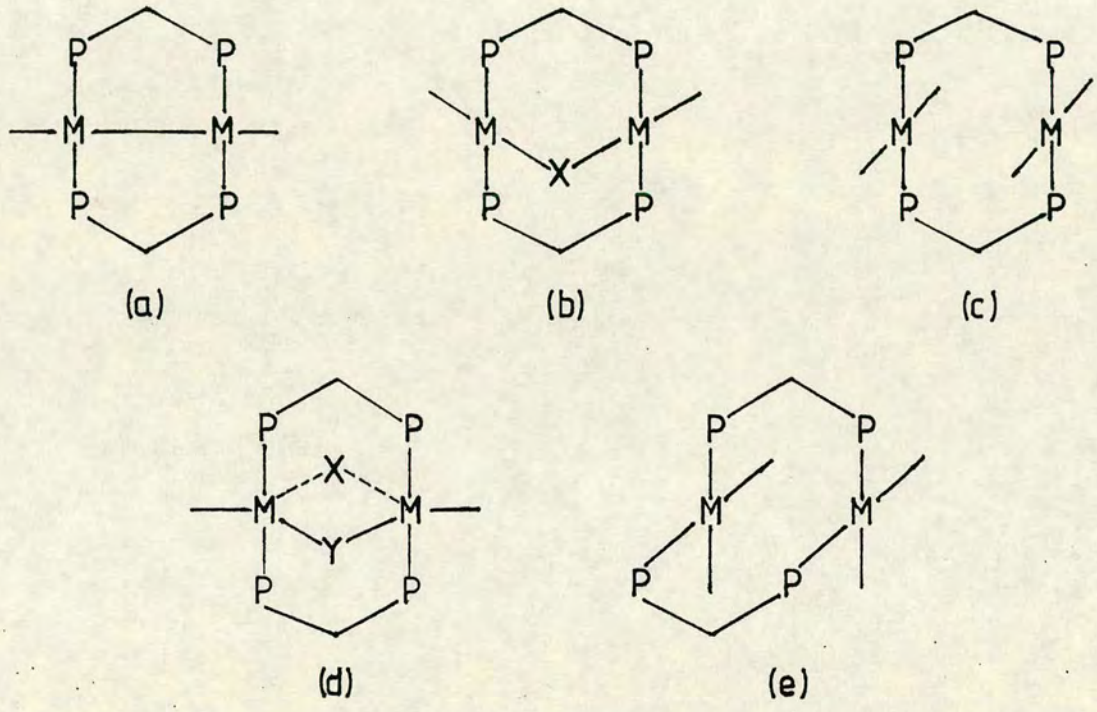
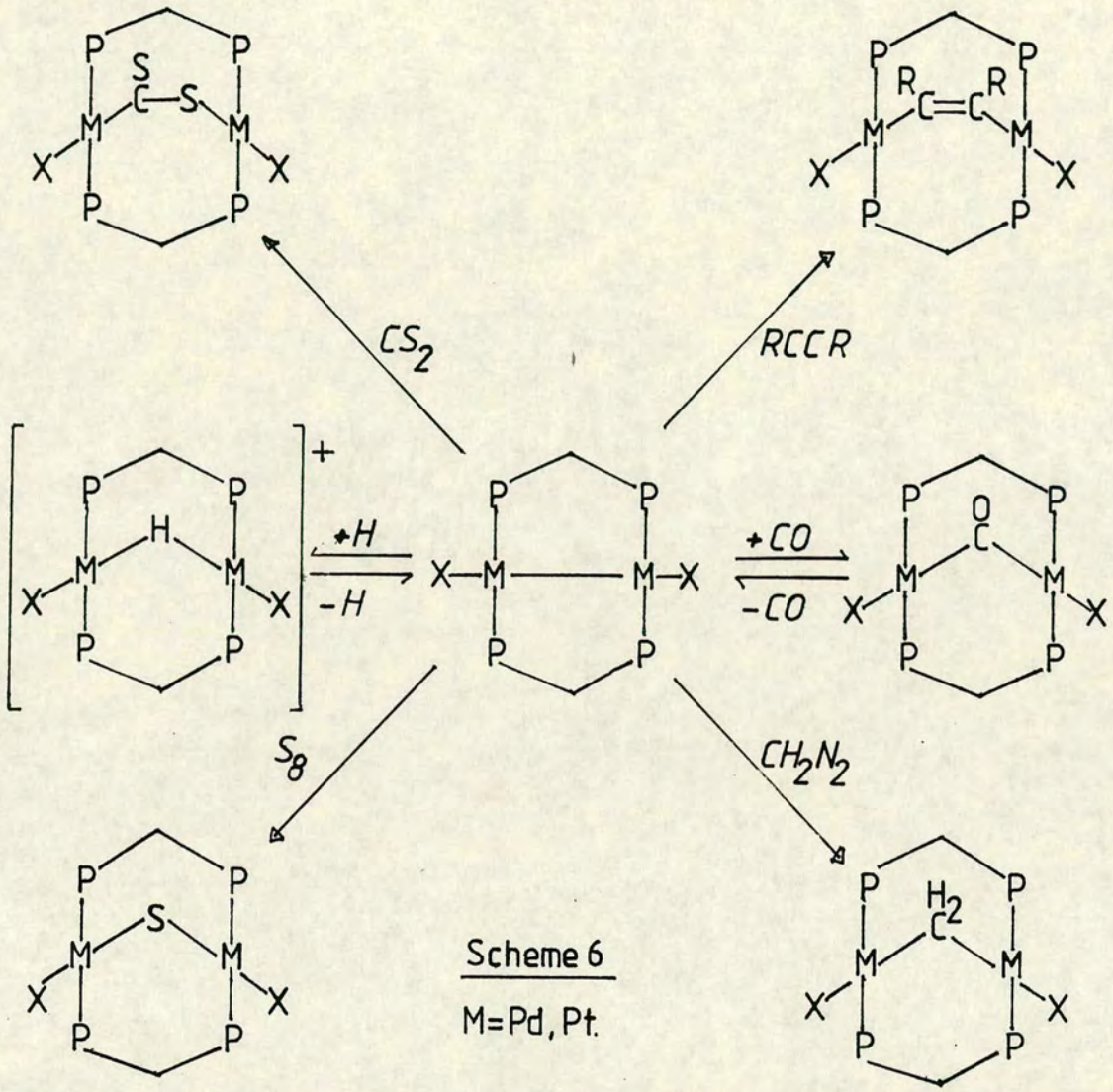


Figure 1: Common orientations of bridging dppm ligands in bimetallic complexes

In these complexes the metal centres are constrained in close proximity (2.1-3.3Å) by the two diphosphine ligands. The option of facile metal-metal bond formation or rupture within the stable '$M(PCH_2P)_2M$' framework has allowed new routes to bimetallic species to be explored and new substrate coordination modes identified [Scheme 6].



Scheme 6

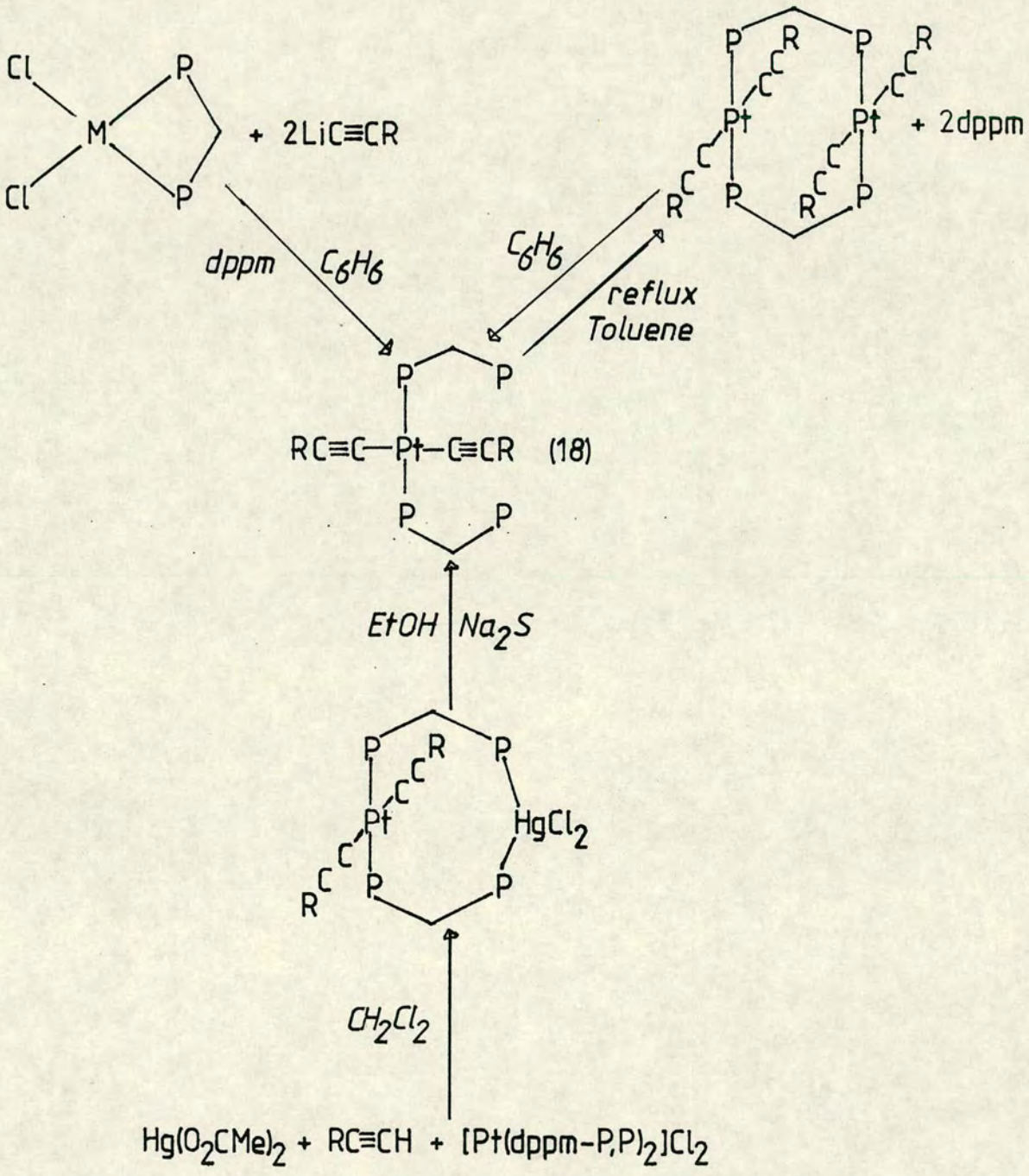
M=Pd, Pt.

In recent years several routes to heterobimetallic complexes have been developed which exploit the propensity of dppm to function as a bridging ligand. Some of these methods are discussed in the following section.

1.4.1 THE USE OF METAL COMPLEXES CONTAINING MONODENTATE DPPM

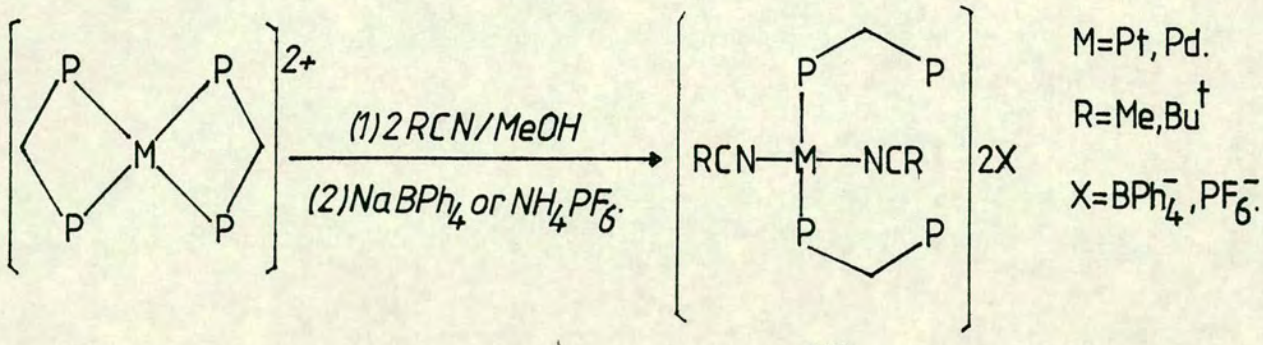
This route to heterobimetallic complexes is used in Chapters 4 and 5 for a variety of diphosphine ligands and is an approach utilised by Shaw and co-workers[44-59,182]

Bis(monodentate dppm) complexes of the type trans-$[MX_2(dppm\text{-}P)_2]^{n+}$ (M=Pt or Pd; n=0, X=C≡CR; n=2, X=CNR; n=0, X=CN) have been prepared as outlined in Equations [14-16]. The choice of ligand X, acetylide, isonitrile or cyanide, is important since they must be strongly bonding to platinum or palladium and have a preference for mutually-trans coordination.



44,45.

----------[14]



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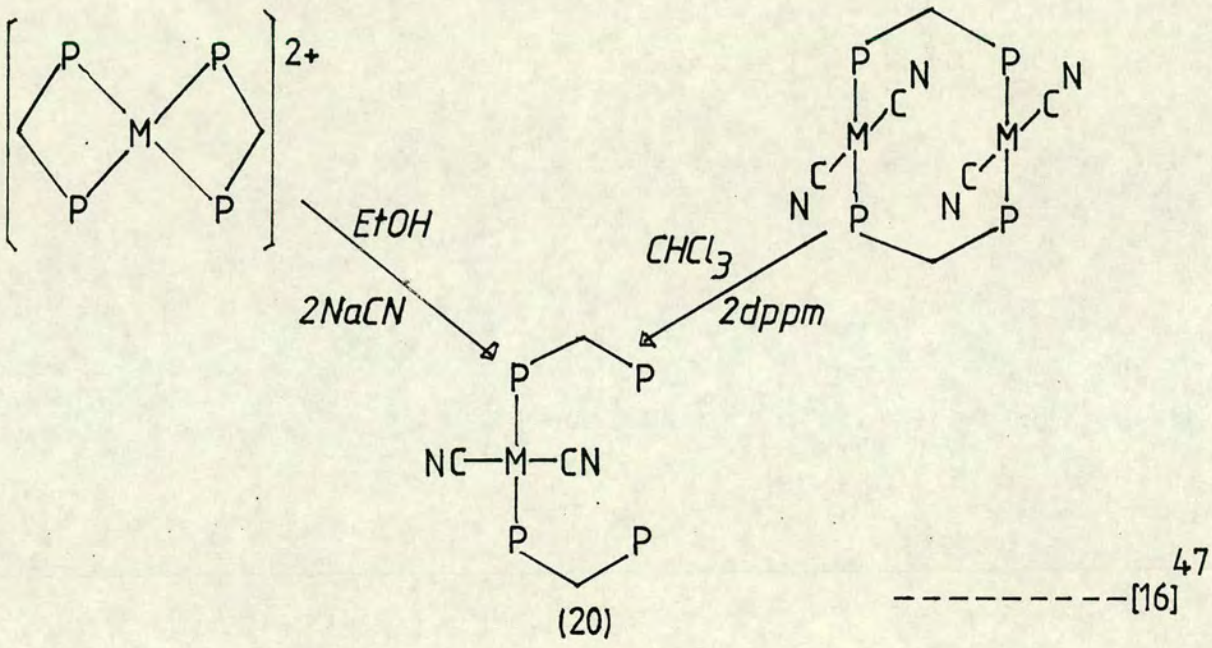
---------[15]



47

---------[16]

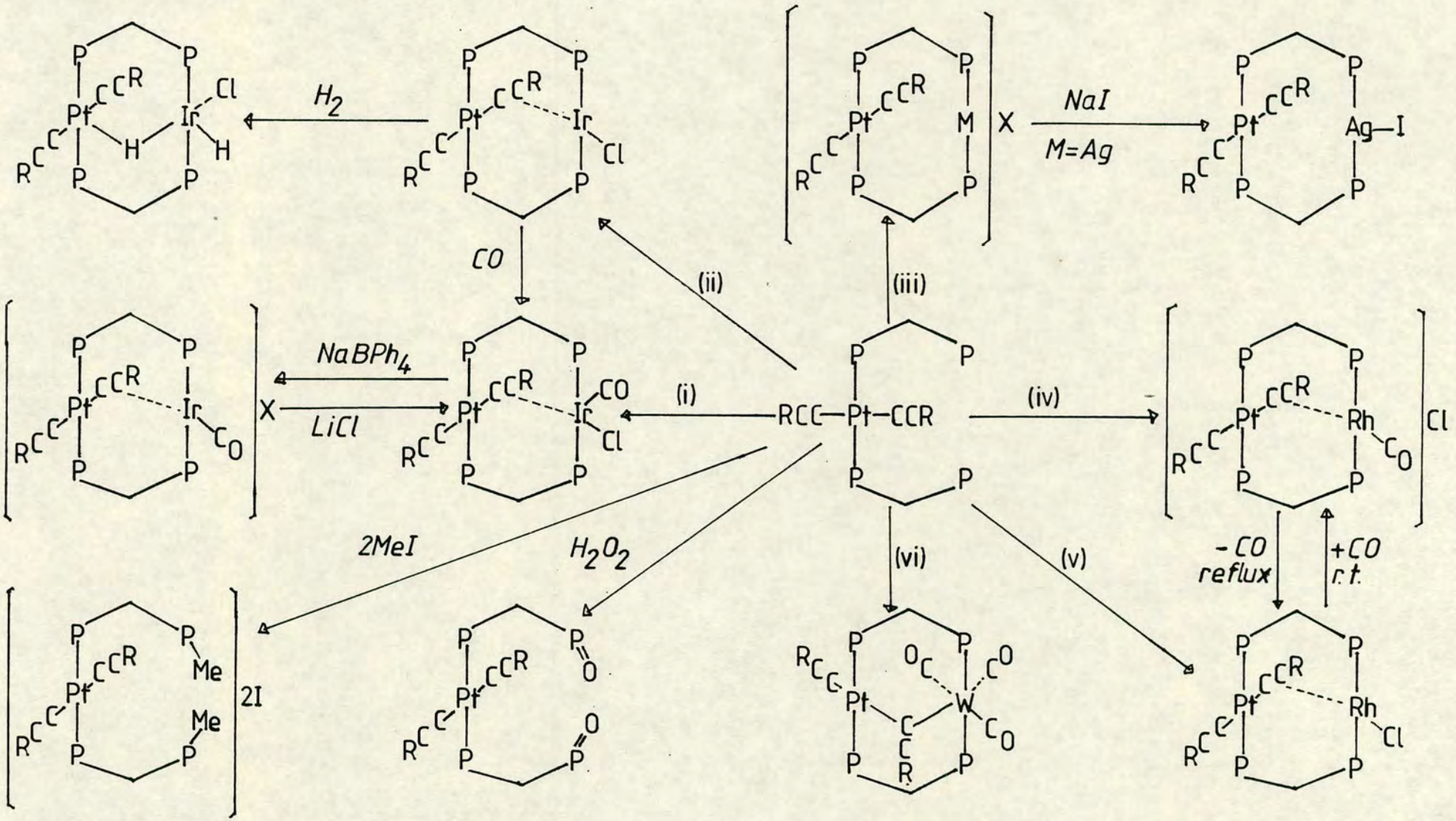
The $^{31}P-\{^{1}H\}$ n.m.r. spectra for (18-20) are broad at room temperature but at low temperature sharpen to reveal AA'BB' type spectra corresponding to the static structures. This variable-temperature behaviour is interpreted as rapid 'end over end' exchange by dppm ($Ph_2PCH_2\overset{*}{P}Ph_2Pt \rightleftharpoons Ph_2\overset{*}{P}CH_2PPh_2Pt$) at ambient temperature, which is halted at low temperatures. An impressive chemistry has been developed for these <u>trans</u>-$[MX_2(dppm\text{-}P)_2]^{n+}$

complexes pertaining to the systematic preparation of heterobimetallic complexes. Some reactions of $[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$ (18) with various transition metal substrates and reagents are illustrated in Scheme 7.

In some cases the heterobimetallic complex is only one of several reaction products and cannot be separated to the pure, desired complex. This is true for $[(RC{\equiv}C)Pt(\mu\text{-}C{\equiv}CR)(\mu\text{-}dppm)_2M(CO)_3]$ (21) (M=Cr,Mo,W), which are produced together with the 'face to face' (Figure 1, type c) binuclear complex $[Pt_2(\mu\text{-}dppm)_2(C{\equiv}CR)_4]$ by the method shown (Scheme 7). A better method for the preparation of (21) is by a transmetallation reaction involving the readily accessible Pt-Ag heterobimetallic $[(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgX]$ (X=Cl,I), which on treatment with $[Mo(CO)_3(cht)]$, $[W(CO)_3(NCMe)_3]$ or $[Cr(CO)_4(nbd)]$ gives (21) in high yield as the sole bimetallic product[51]. Similarly $[(RC{\equiv}C)Pt(\mu\text{-}dppm)_2(\sigma,\eta\text{-}C{\equiv}CR)Rh(CO)]^+$ is best prepared from the Pt-d[10] metal complexes $[(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2ML_n]^{n+}$ (n=0, ML_n=$HgCl_2$, AgCl, CuI; n=1, M=Au) and $[Rh_2Cl_2(CO)_4]$[52].

Characterisation of the products in Scheme 7 has included microanalysis, i.r. and multinuclear n.m.r. spectroscopy and X-ray structure determinations have confirmed the formulations $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgI]$[53], $[(p\text{-}MeC_6H_4C{\equiv}C)Pt(\mu\text{-}C{\equiv}CC_6H_4Me\text{-}p)(\mu\text{-}dppm)_2W(CO)_3]$[51] and $[(MeC{\equiv}C)Pt(\mu\text{-}dppm)_2(\sigma,\eta\text{-}C{\equiv}CMe)Rh(CO)]PF_6$[52].

<u>trans</u>-$[(RCN)_2M(dppm\text{-}P)_2]^{2+}$ (19) and in particular <u>trans</u>-$[(CN)_2M(dppm\text{-}P)_2]$ (20) (M=Pd,Pt) also form heterobimetallics with Ag(I), Au(I), Hg(II), Mo(0), Rh(I) and Ir(I),

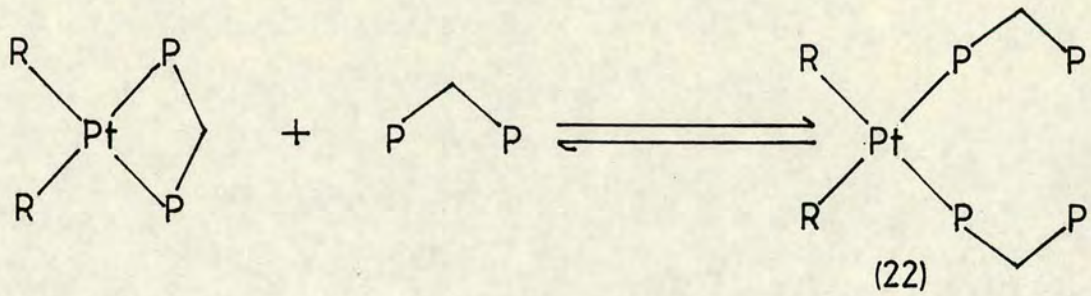


Scheme 7 Chemistry of trans-$[Pt(C{\equiv}CR)_2(dppm\text{-}P)_2]$

(i) $[IrCl(CO)(PPh_3)_2]$ (ii) $[Ir_2Cl_2(C_8H_{14})_4]$ (iii) $[AgNO_3]$, $[AuClPPh_3]$ (iv) $[Rh_2Cl_2(CO)_4]$ (v) $[Rh_2Cl_2(C_8H_{14})_4]$ (vi) $[W(CO)_3(MeNC)_3]$

which closely resemble the heterobimetallic systems produced from trans-$[(RC{\equiv}C)_2Pt(dppm\text{-}P)_2]$ (18)[46,47,54].

Shaw and co-workers have also synthesised bis(monodentate dppm) complexes of the type cis-$[PtR_2(dppm\text{-}P)_2]$ (22)(R=alkyl, aryl). Treatment of cis-$[PtCl_2(dppm\text{-}P,P)]$ with a Grignard or lithio-reagent gives cis-$[PtR_2(dppm\text{-}P,P)]$ which on mixing with an equimolar quantity of dppm sets up the equilibrium shown in Equation [17].



(22)

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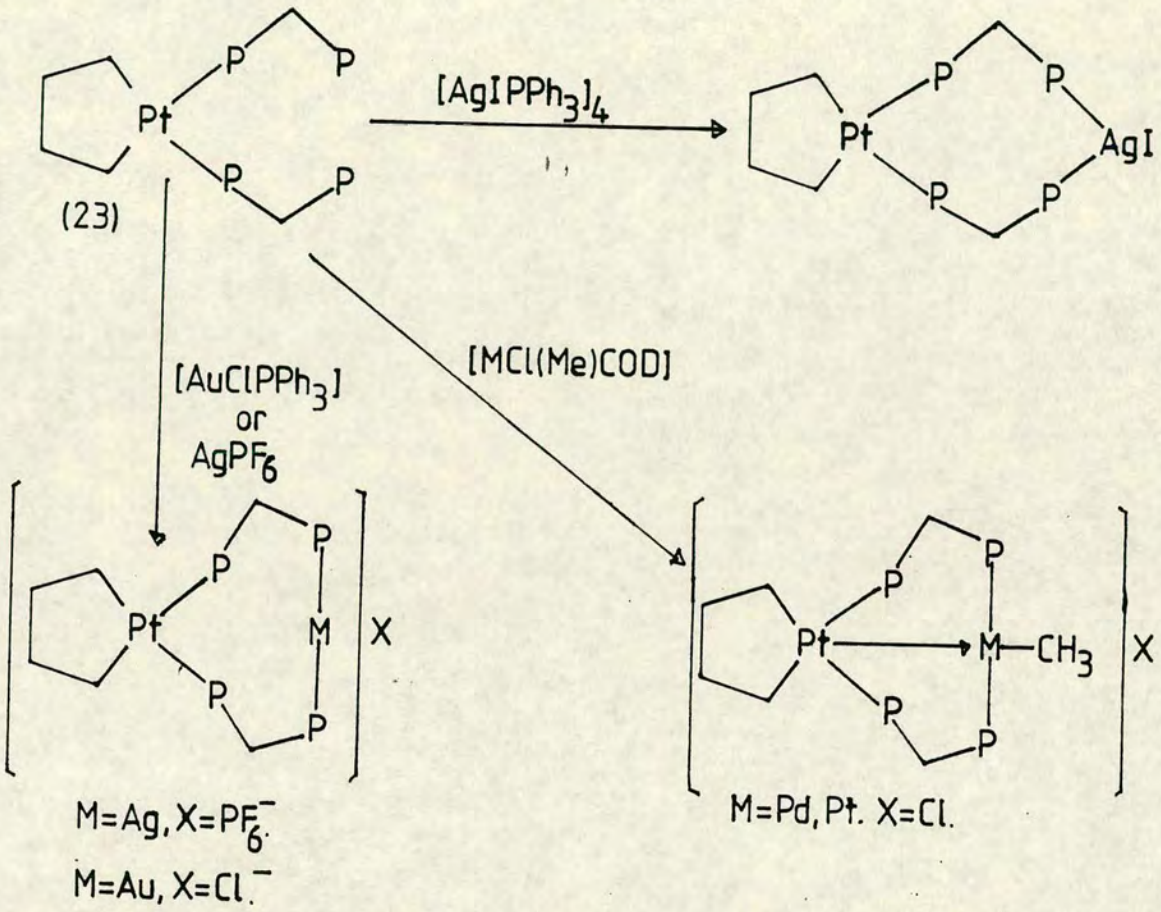
Working at high concentrations and low temperatures shifts the equilibrium in favour of the bis(dppm-P) complex (22). This allows isolation of $[R_2Pt(dppm\text{-}P)_2]$ (R=Me,o-tolyl 1-naphtha) which under appropriate conditions can be used to synthesise heterobimetallic compounds[55,56]. However the most robust system of the type (22) against dissociation is the bis(dppm-P) platinacycle $[\overline{Pt(CH_2CH_2CH_2CH_2)}(dppm\text{-}P)_2]$ (23) produced from 1,4-dilithiobutane and $[PtCl_2(dppm\text{-}P,P)]$ with subsequent treatment with dppm. The complex (23) is a convenient starting material for preparing bimetallics as illustrated in Scheme 8 [57].

As expected the cis-configuration in (22) and (23)

produces bimetallics with larger M-M separations (M-M=4.91Å, syn-$[(C_6H_4Me\text{-}o)_2Pt(\mu\text{-dppm})_2PtMe_2]$[56]; 4.36Å, cis,cis-$[Me_2Pt(\mu\text{-dppm})_2PtMe_2]$[58]) compared to separations found for the bimetallics synthesised from the trans-complexes (18-20) (M-M=3.18Å, $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgI]$[53]; 3.04Å $[(p\text{-tolyl})_2Pt(\mu\text{-dppm})_2W(CO)_3]$[51]; 3.07Å $[(MeC{\equiv}C)_2Pt(\mu\text{-dppm})_2Rh(CO)]PF_6$[52]).

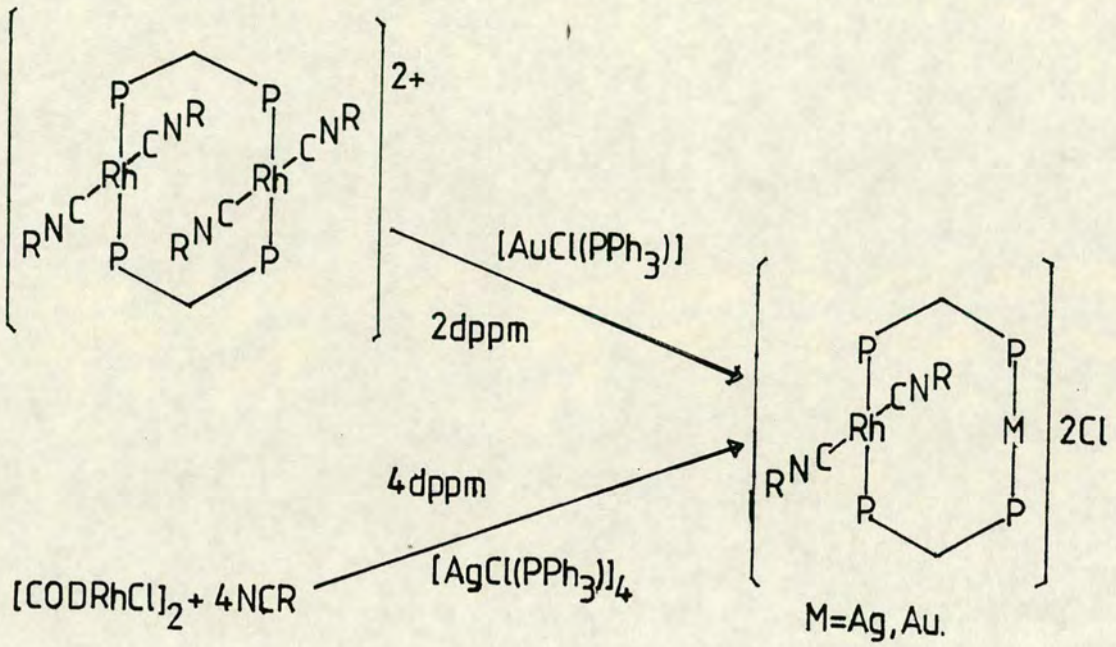


Scheme 8: Reactions of $[\overline{Pt(CH_2)_3CH_2}(dppm\text{-}P)_2]$ (23)

Monodentate dppm systems have been developed for metals other than Pt and Pd. Treatment of the 'face to face' bimetallic $[Rh_2(CNBu^t)_4(\mu\text{-dppm})_2]Cl_2$ with 4 equivalents of dppm in CH_2Cl_2 produced a fluxional system identified by low temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy as the tris-

(monodentate dppm) complex $[Rh(CNBu^t)_2(dppm\text{-}P)_3]Cl$.

Attempts to isolate this complex or its Ir analogue failed. However heterobimetallics of the type $[(CNR)_2Rh(\mu\text{-}dppm)_2M]2X$ (M=Ag,Au) can be prepared from either $[Rh_2(CNBu^t)_4(\mu\text{-}dppm)_2]2Cl$ and 2dppm or by a 'one-pot' synthesis [Equation 18] [59].



---------[18]

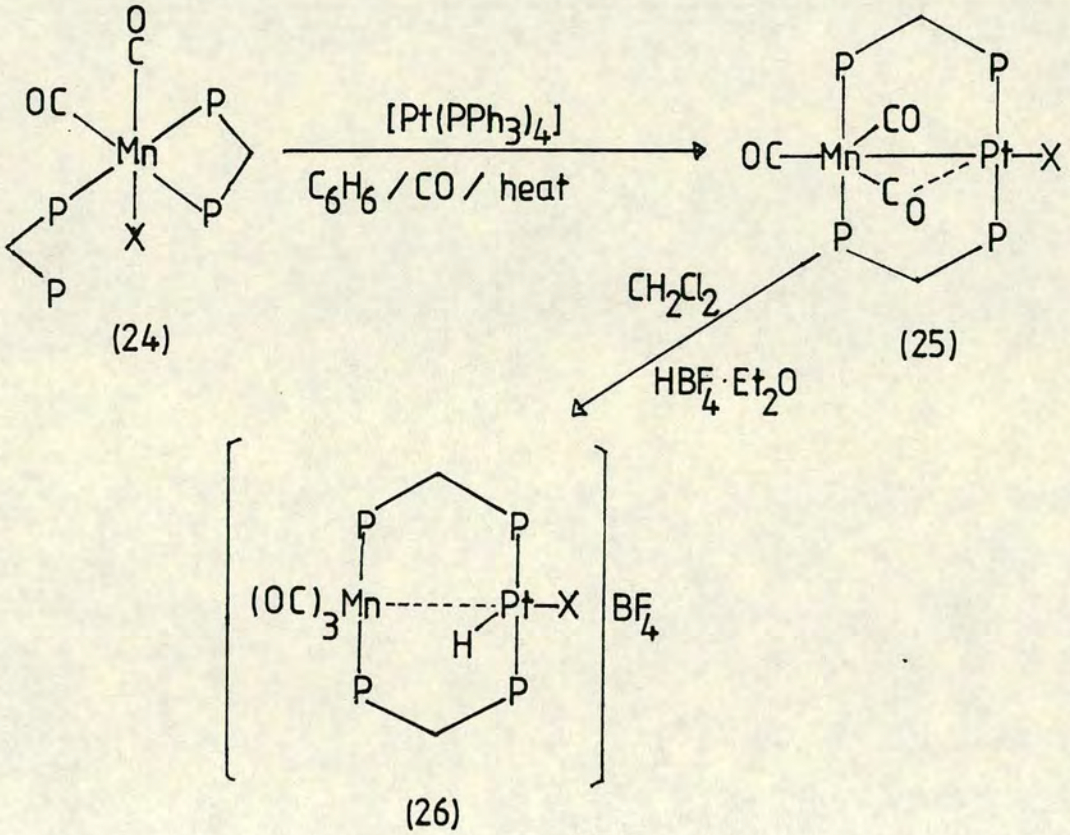
Very recently the bis(diphenylarsino)methane (dpam) complexes cis-$[PtMe_2(dpam\text{-}As)_2]$ and trans-$[PtX_2(dpam\text{-}As)_2]$ (X=Cl,Br) have been identified and the latter used to prepare bimetallic complexes such as trans-$[Cl_2Pt(\mu\text{-}dpam)_2HgCl_2]$ and $[ClPt(\mu\text{-}dpam)_2PtCl]$ [179].

1.4.2 FORMATION OF HETEROBIMETALLIC COMPLEXES INVOLVING RING OPENING OF A 4-MEMBERED CHELATE RING M(dppm-P,P)

Considerable ring-strain exists when dppm chelates to a metal ($\overline{MPCP}$) as attested by low $P\hat{M}P$ (~70° cf. normal 90°) and $P\hat{C}P$ (~95° cf. normal 109°) angles[60]. As a result, 'ring-opening' reactions with subsequent M' coordination

have been used as a viable route to dppm bridged hetero-bimetallics. Already in Section 1.4.1 there are several examples of the metal coordination mode for dppm changing from chelating to dangling when additional ligands are introduced [Equations 14-17].

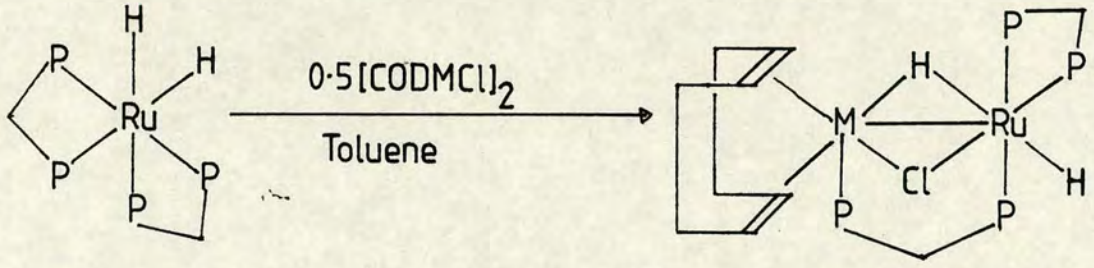
Treatment of the bis(chelate) salt $[Pt(dppm\text{-}P,P)_2]2Cl$ with an equivalent of HgX_2 (X=C≡CR,CN) in ethanol or with AgOAc/2PhC≡CH in CH_2Cl_2 gives the heterobimetallics $[(X)_2Pt(\mu\text{-}dppm)_2ML_n]$ (ML_n=$HgCl_2$, X=C≡CR,CN; ML_n=AgCl, X=C≡CR)[61]. The manganese complex cis,mer-$[MnX(CO)_2(dppm\text{-}P,P)(dppm\text{-}P)]$ (24) (X=Cl,Br) if treated with $[Pt(PPh_3)_4]$ by a combined ring-opening/redox process gives the Mn(O)-Pt(I) complex $[(OC)_3Mn(\mu\text{-}dppm)_2PtX]$ (25). An extensive chemistry has been reported for (25)[62] which includes treatment with $HBF_4.Et_2O$ to give the cationic hydride complex $[(OC)_3Mn(\mu\text{-}dppm)_2PtH(X)]BF_4$ (26) [Equation 19], the crystal structure of which (X=Br) has been determined[63].



(24) (25) (26)

---------[19]

The Pd(I) analogue of (25) has been prepared either by a 'one-pot' synthesis with $[MnX(CO)_5]$ (X=Cl,Br) and $[Pd(dba)_2]$ in the presence of dppm[64] or by treating $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with $Na[Mn(CO)_5]$[65]. The Group 6 metal carbonyl derivatives fac- or mer-$[(CO)_3M(dppm\text{-}P,P)(dppm\text{-}P)]$[66,67] (M=Cr,Mo,W) also undergo ring-opening reactions with Rh or Ir carbonyl complexes[68] and the mer-isomer reacts with trans-$[PtH(X)(PPh_3)_2]$ to give the neutral product $[(OC)_3M(\mu\text{-dppm})_2PtH(X)]$[69]. The reaction of cis-$[RuH_2(dppm\text{-}P,P)_2]$ with $[CODMCl]_2$ (M=Rh,Ir) gives the novel heterobimetallic (27) which retains a chelating dppm ligand on ruthenium[70] [Equation 20].



(27)

---------[20]

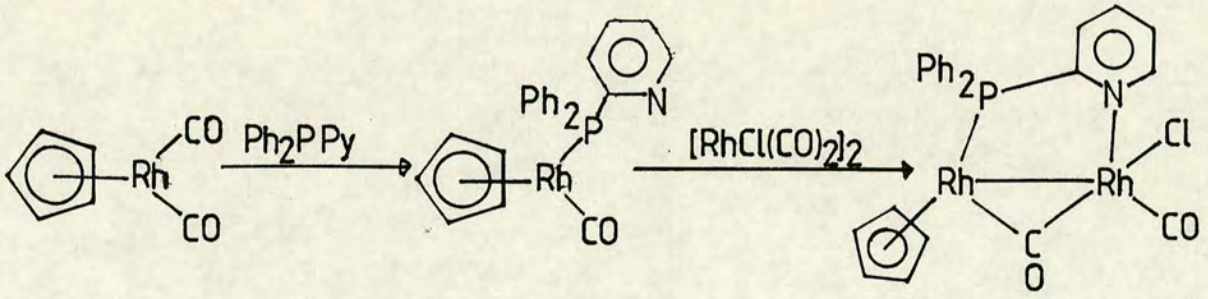
Ring-opening reactions leading to heterobimetallic formation have also been reported for the complexes trans-$[OsX_2(dppm\text{-}P,P)_2]$ (X=Cl,Br)[71] and $[M(CO)(dppm\text{-}P,P)_2]Cl$ (M=Rh,Ir)[72].

1.4.3 HETEROBIMETALLICS FORMED USING HETERODIFUNCTIONAL LIGANDS

New ligands containing different donor functions are rapidly being developed as a means whereby two distinctly different metals, for example a first row and either a

second or third row transition metal, can be incorporated in a single complex in close proximity. To date, it appears that this route to heterometallic complexes has not yet been fully exploited; undoubtably due to the practical difficulties of producing the heterodifunctional ligands.

2-(Diphenylphosphino)pyridine (PPh_2Py) forms complexes with the Platinum group metals in which it preferentially coordinates through the phosphorus atom. The uncoordinated pyridine nitrogen is then available to bind a second metal. [Equations 21 and 22].



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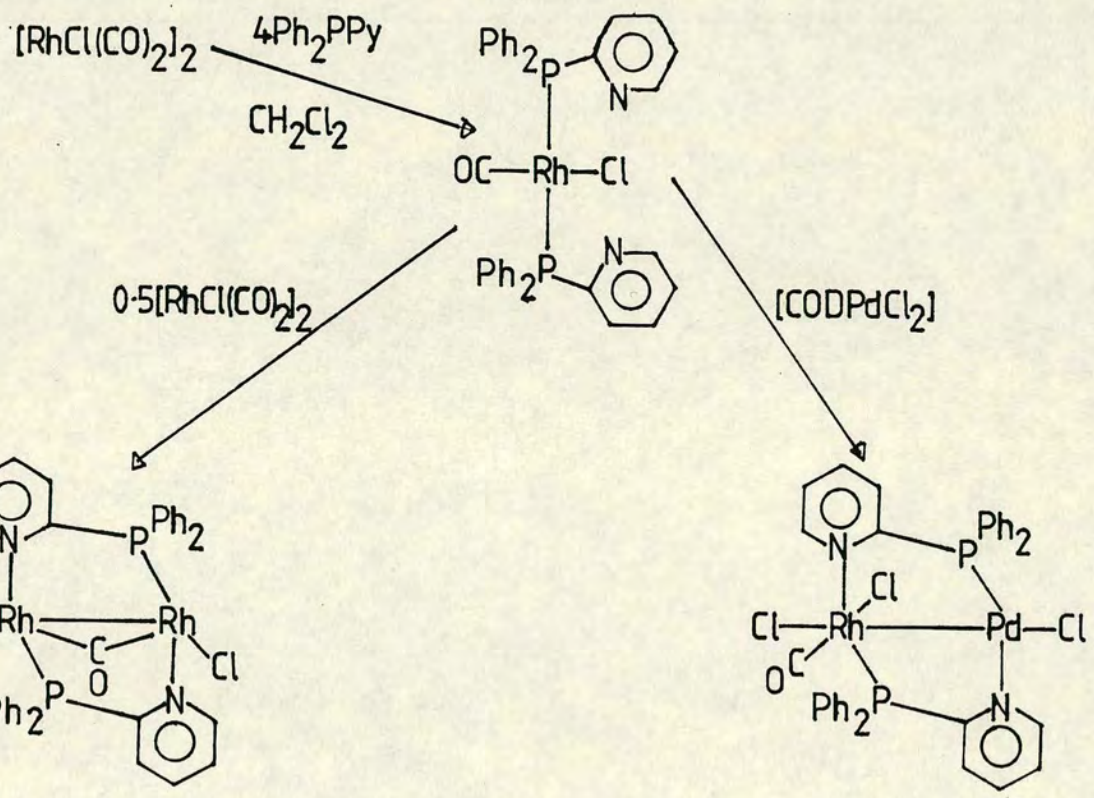
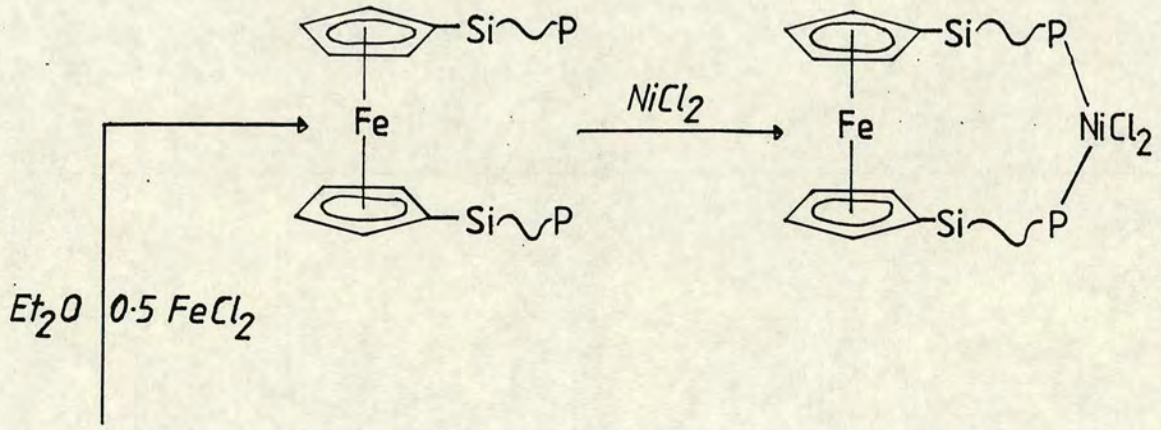


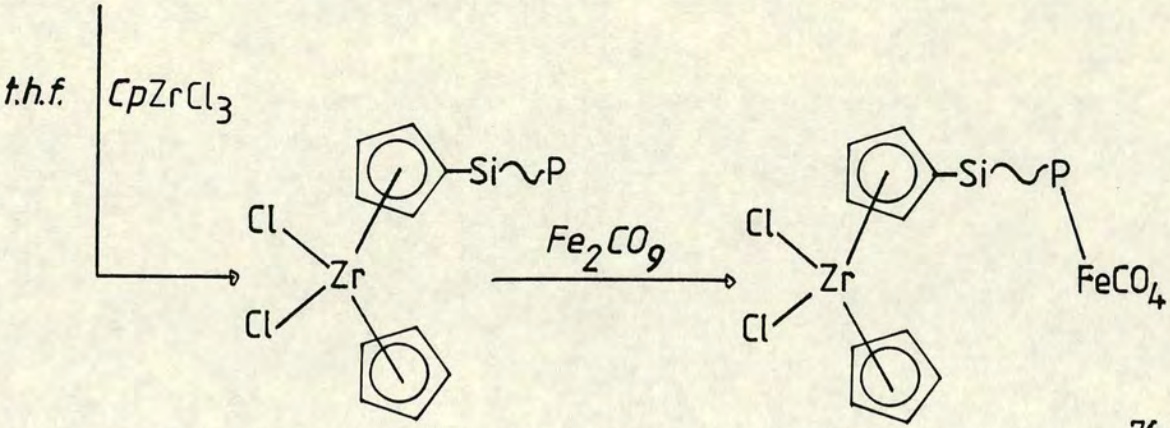
74,75

---------[22]

The complexes cis-$[MCl_2(Ph_2\underline{P}py)_2]$ (M=Pd,Pt) and cis,cis,trans-$[RuCl_2(CO)_2(Ph_2\underline{P}py)]$ have also been prepared. Although there are structural similarities between bis-(μ-dppm) and bis(μ-Ph_2Ppy) complexes [Fig.1] insertion of small molecules into the M-M bond of the latter does not occur. The lack of flexibility in the Ph_2Ppy bridging ligand and its inability to span M-M separations of greater than 3Å are thought responsible for this inactivity[42].

The ligands $Li[(C_5H_4)SiMe_2.CH_2PPh_2]$[76] and $Tl[(C_5H_4)-(CH_2)_nPPh_2]$ (n=0,2)[77] can be used to form substituted cyclopentadienyl complexes of Fe, Ti and Zr. These when treated with a suitable metal carbonyl or metal halide use the P atom of the pendant group to coordinate a second metal fragment [Equations 23 and 24].





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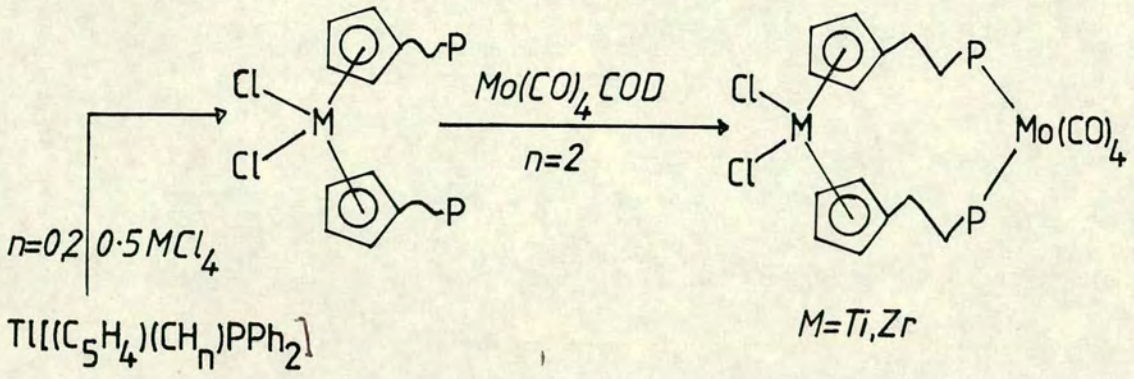

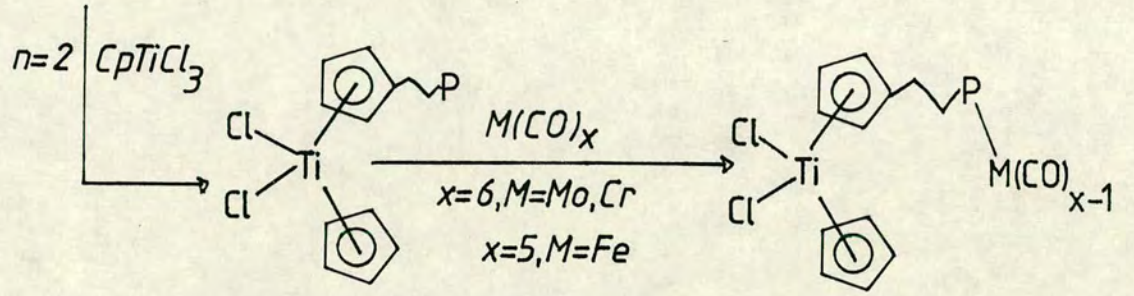

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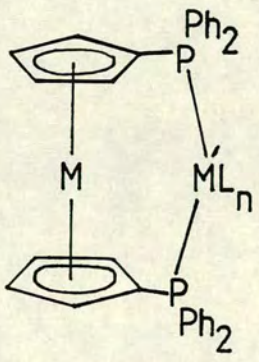
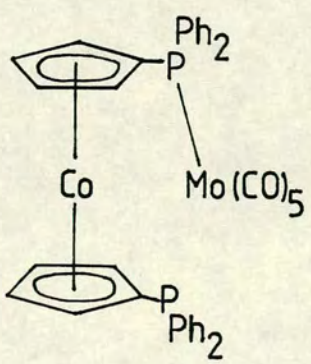
--------[24]

The ferrocene and cobaltocene derivatives $[Fe(C_5H_4PPh_2)_2]$[78] and $[Co(C_5H_4PPh_2)_2]$[79], prepared by treatment of the metal halide with $Tl(C_5H_4PPh_2)$, are also convenient precursors for the preparation of heterobimetallic systems. Many of the structures of the heterobimetallics have been confirmed by single-crystal, X-ray studies (28 and 29).



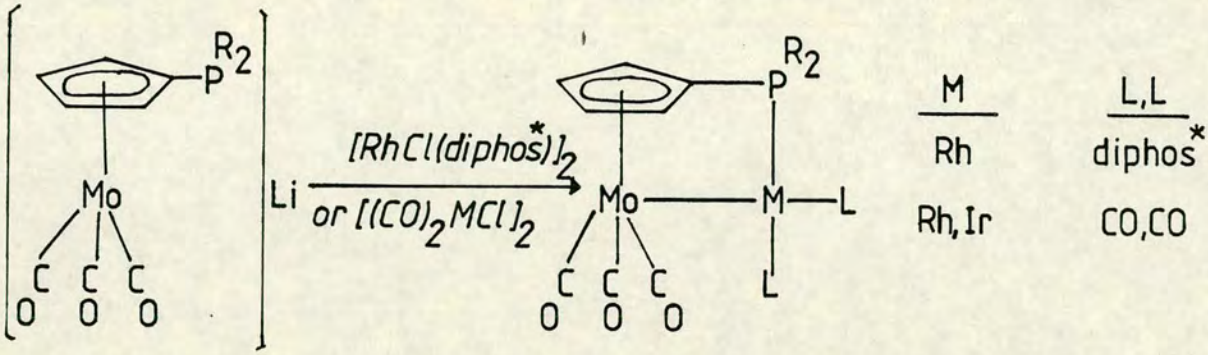
(28)

M	M'Ln
Co	$Mo(CO)_4$
Fe	$NiBr_2$
Fe	$PdCl_2$
Fe	$Mo(CO)_4$



(29)

The anionic half-sandwich complex $Li[(C_5H_4P(C_6H_4Me\text{-}p)_2)\text{-}Mo(CO)_3]$ has also been prepared. When treated with 0.5 mole equivalents of $[RhCl(diphos^*)]_2$ or $[(CO)_2MCl]_2$ (M=Rh,Ir) heterobimetallics are formed containing a M-M bond[80] [Equation 25].



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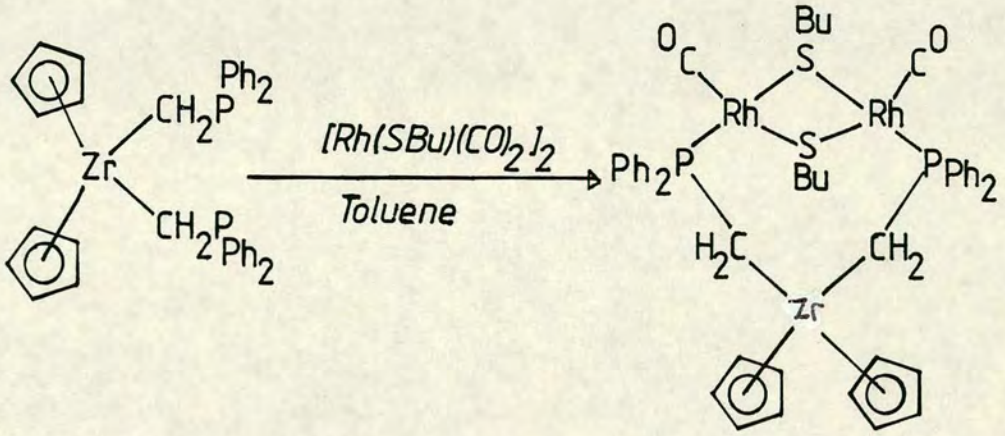
Interest in Rh/Zr heterobimetallic complexes stems from the use of Rh dispersed on a ZrO_2 support as a highly selective Fischer-Tropsch catalyst for a variety of α-olefin feedstocks[81]. A systematic preparation of useful homogeneous model compounds involves preparation of a Zirconium complex with ligands containing P donor atoms which subsequently bind a Rh fragment [Equations 26 and 27].



[82]
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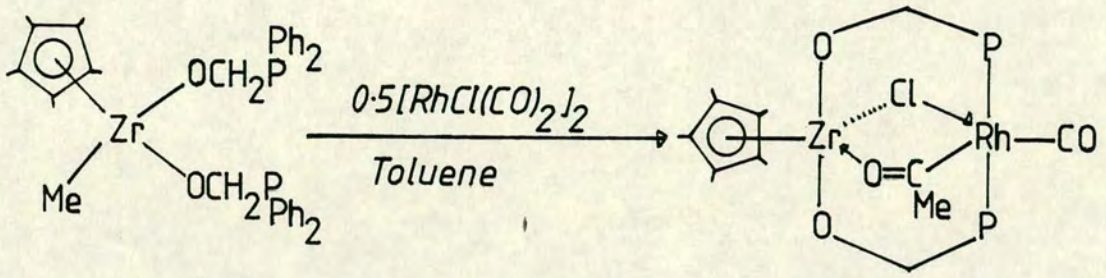

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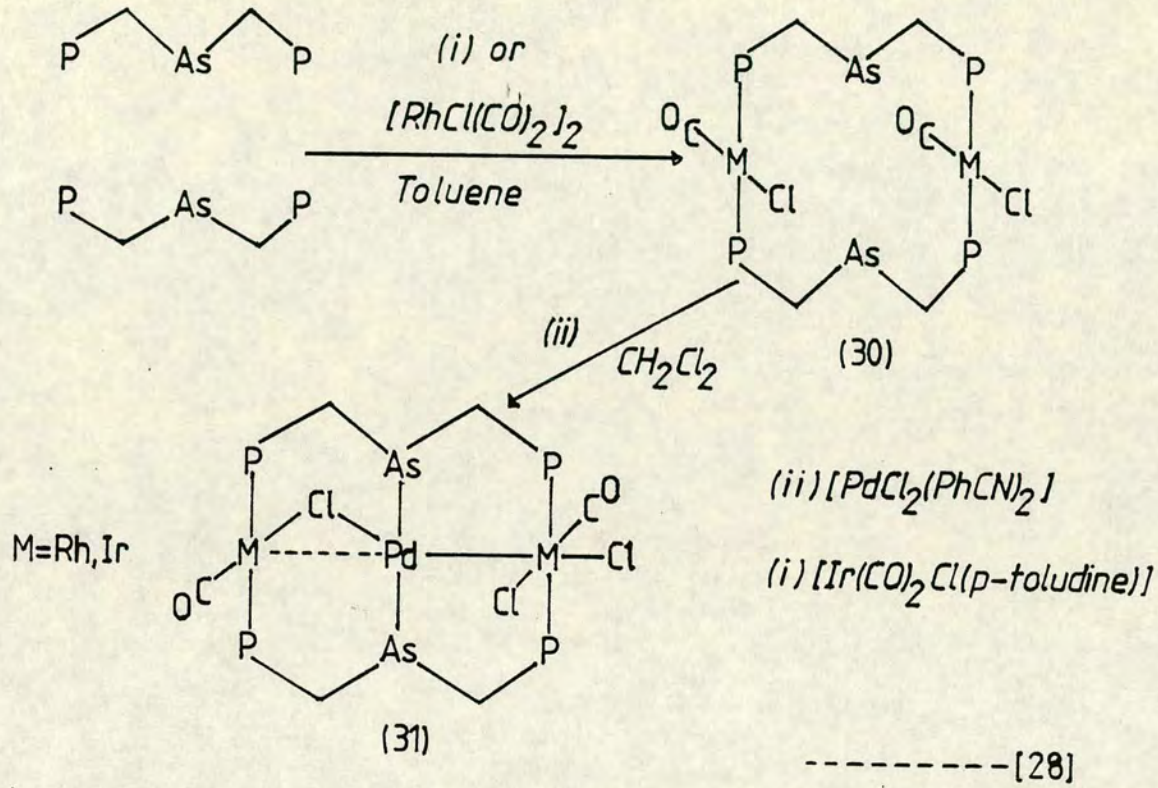
--------[27]

1.5 ROUTES TO LARGE HETEROMULTIMETALLIC COMPLEXES

Increasingly multi-dentate ligands are being designed so that several metals can be located in close proximity. This can result in multicentre M-M interactions and may provide the option of several coordination sites for probe molecules - thus more closely modelling an active metal surface.

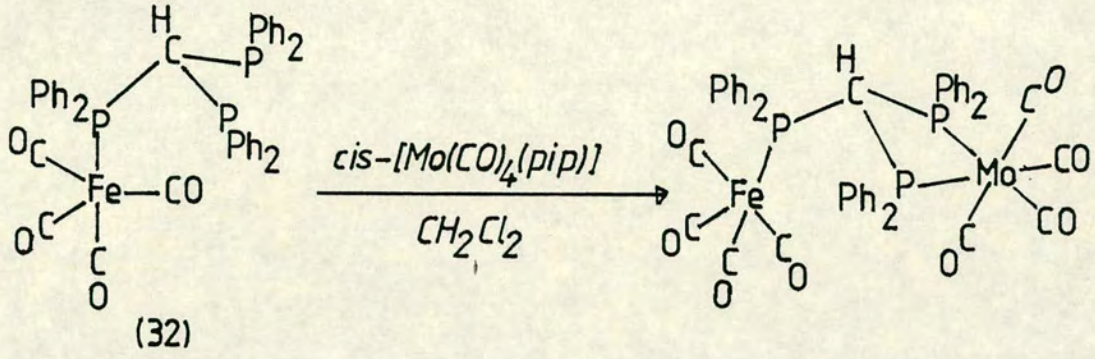
Bis[(diphenylphosphino)methyl]phenylarsine (dpma) on treatment with 0.5 equivalents of $[RhCl(CO)_2]_2$ in toluene yields the metallomacrocycle $[Rh_2(CO)_2Cl_2(\mu\text{-dpma})_2]$ (30). A further metal ion can be located in the central cavity of (30). Thus treatment with $[PdCl_2(PhCN)_2]$ followed by methanolic $NaBPh_4$ precipitates the product $[Rh_2Pd(CO)_2Cl_3(\mu\text{-dpma})_2]$ (31) [Equation 28]. Both (30, M=Rh) and (31, M=Rh) have been examined by X-ray crystallography. In (31, M=Rh) the Pd(II) ion is coordinated by

the two As atoms of the metallomacrocycle and is asymmetrically positioned between the two Rh atoms (Pd-Rh(1) 2.699Å; Pd-Rh(2) 3.166Å)[84].



---------[28]

Finally in this section, the P-donor tripod ligand tris-(diphenylphosphino)methane ($HC(PPh_2)_3$)[85] can be employed for the systematic construction of heterometallic systems. The reaction of $HC(PPh_2)_3$ with either $Fe_3(CO)_{12}$ or $Fe(CO)_5$ in toluene yields several products which can be separated by fractional crystallisation. Two of these products $[HC(PPh_2)_3Fe(CO)_4]$ (32) and $[HC(PPh_2)_3Fe(CO)_3]$ (33) are useful precursors for the synthesis of heterometallic complexes [Equations 29 and 30][86]. Similar, equally useful complexes, $[Mo(CO)_5(HC(PPh_2)_3)]$ and cis-$[Mo(CO)_4(HC(PPh_2)_3)]$ have also been reported[87].



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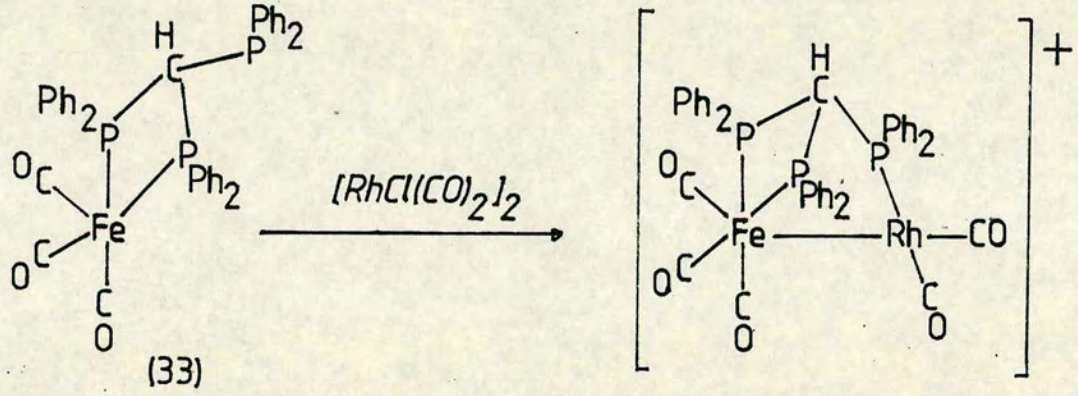

(33)

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CHAPTER 2

REACTION OF PLATINUM COMPLEXES CONTAINING SECONDARY PHOSPHINE CHALCOGENIDE LIGANDS WITH $[CODMCl]_2$ (M=Rh(I),Ir(I))

2.1 INTRODUCTION

In this chapter some of the platinum complexes produced in the reaction of $Pt(S_2CNR_2)_2$ and Ph_2PSH (Scheme 1) are utilised in the construction of Pt(II)/Rh(I) and Pt(II)/Ir(I) heterobimetallic complexes using as a source of Rh(I) or Ir(I) the versatile dinuclear $[CODMCl]_2$ (M=Rh,Ir) systems. For reference the observed $^{31}P-\{^1H\}$ n.m.r. parameters for the platinum ligands (2) and (6-10) are given in Appendix 1.

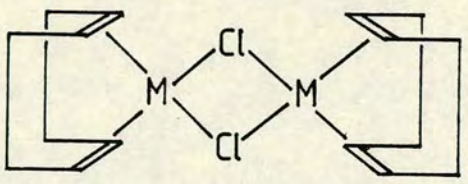
It is no coincidence that chemistry involving rhodium and iridium has developed rapidly in recent years. Many compounds containing these particular metals have proved effective as homogeneous catalysts. The most commonly found oxidation states for organometallic Rh and Ir compounds are M(I) and M(III). It is the facile, frequently reversible couple, particularly for Rh, that is largely responsible for the considerable catalytic activity shown towards organic substrates.

In 1966 Wilkinson and co-workers described the catalyst precursor $RhCl(PPh_3)_3$, which could be used for the selective hydrogenation of olefinic groups at room temperature[88]. Later the inclusion of a chiral bidentate phosphine ligand[89] allowed Rh catalysts to achieve asymmetric transformations in hydrogenation, hydroformylation and hydrosilylation reactions[90]. Many of the catalytic systems utilise alkene complexes such as $[(C_2H_4)_2RhCl]_2$[91] as a starting point. Moreover, incorporating a chelating dialkene such as 1,5-cyclooctadiene (COD) or norbornadiene (NBD) confers

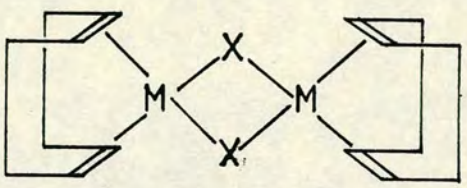
stability to the systems and often allows isolation of the catalyst precursor[92,93]. This more applied work with its long-term prize of industrial exploitation has been complimented by fundamental research into the coordination chemistry of Rh and Ir. Several species such as $RhCl(PPh_3)_3$,[88] $RhCl(CO)(PPh_3)_2$[94], $IrCl(CO)(PPh_3)_2$[95] and $[(C_5Me_5)RhCl_2]_2$[96,97] can be pinpointed as materials that display a rich and diverse chemistry. Similarly notable compounds, which are used extensively in this chapter, are $[CODRhCl]_2$ (34) and $[CODIrCl]_2$ (35). Some chemistry of (34) and (35) is now described.

2.2.1 CHEMISTRY OF $[(COD)MCl]_2$ (M=Rh (34), M=Ir (35))

$[(COD)RhCl]_2$ (34) is obtained as an air stable orange solid by refluxing $RhCl_3.3H_2O$ with 1,5-COD in an ethanol/water mixture for 3 hours[98]. A refluxing period of 24 hours is required to generate the bright-red iridium analogue (35)[99].



(34) M=Rh (35) M=Ir

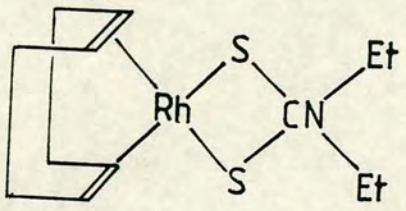


(36)

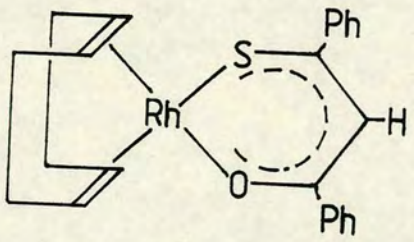
Replacement of the chloride bridges by alternative bridging groups X (36) is a recurring theme in the chemistry of (34) (X=Br,I[98], SCN[100], N_3[101], OMe, O_2CMe[98], C_2O_4[102], SPh[103,104]

PPh_2,[105] PPhMe[106]) and (35)[105-112].

Of greater relevance to the work described in this chapter are the bridge cleavage reactions of (34) and (35) with bidentate ligands containing the group 6 donor atoms O and S. There are examples of neutral, anionic and dianionic dithio ligands bridge-cleaving $[CODRhCl]_2$ to produce monometallic species. Neutral dithio ligands ($S\frown S$) ($S\frown S = Ph_2P(S)CH_2(S)PPh_2$[113], $(MeS)_2(CH_2)_3$, $(Bu^tS)_2(CH_2)_2$[114]) react with (34) in the presence of $AgClO_4$ to give cationic derivatives of the type $[CODRh(S\frown S)]ClO_4$. Treatment of (34) in C_6H_6 with $(S\frown S)^-$ ($S\frown S = S_2P(C_6H_{11})_2^-$; $S_2P(OPh)_2^-$ [115]) and displacement of both pyridine ligands from $[CODRh(py)_2]^+$ by $(S\frown S)^-$ ($S\frown S = S_2CNEt_2^-$) yields the neutral species $[CODRh(S\frown S)]$ ((37), $S\frown S^- = S_2CNEt_2^-$)[103]. Reaction of $S_2C_2(CN)_2^{2-}$ with (34) produces the anionic complex $[CODRh(S_2C_2(CN)_2)]^-$, conveniently isolated as a tetraalkylammonium salt[116].



(37)



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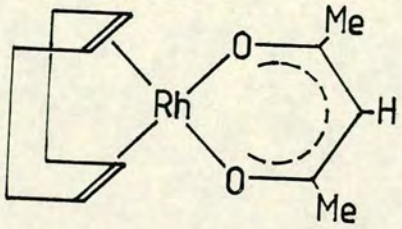
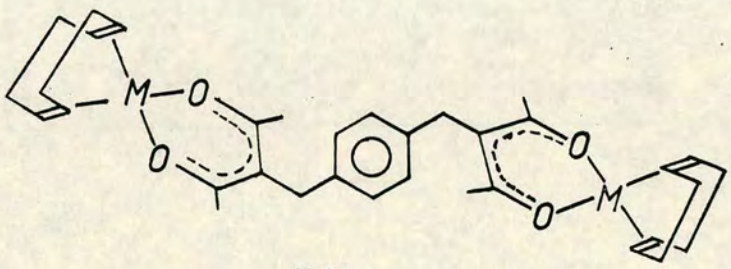


(39)

The reaction of (34) with Tl(SDBM) (SDBM=3-thio-1,3-diphenylprop-2-en-1-one) gives the complex [CODRh(SDBM)] (38). The ^{1}H n.m.r. spectrum of (38) shows separate olefinic resonances for the trans-S and trans-O protons in the coordinated 1,5-COD ligand[117]. If $[(OC)_2RhCl]_2$ and acacH are mixed in the presence of a base the complex $[(OC)_2Rh(acac)]$ is formed. On treatment with 1,5-COD this liberates two equivalents of CO to produce [(COD)Rh(acac)] (39)[118]. The bis(acacH) ligand p-xylene-bis(3-(2,4-pentanedione)) reacts with (34) and (35) in a 1:1 molar ratio to give the homobimetallics (40). The flexibility of the ligand framework allows a facile face to face approach of the metal centres (4Å by molecular models) providing the option of substrate coordination between the metals[119].



(40)

An extensive chemistry exists involving the reaction of ligands containing the group 5 donor atoms N and P with (34) and (35). As briefly mentioned in Chapter 1, considerable effort has been directed toward the synthesis and study of compounds of the type $[(Dialkene)Rh(P\frown P)^*]^+$

(Dialkene = COD,NBD; $(\overset{\frown}{P\ P})^*$ = chiral chelating diphosphine) in the field of homogeneous catalysis and several comprehensive reviews of this topic have been published[120]. The reaction of (34) and (35) with monodentate N,P and As donor ligands gives compounds of the type [CODMClL] and $[CODML_2]^+$ depending on the polarity of the reaction solvent.

There are several examples of heterobimetallics containing an 'M-M' bond and an '$MCOD^+$' fragment, including compound (27) in Equation [20][70]. Reaction of $[(OC)_5Cr-(^tBu_2PLi)]$, formed <u>in situ</u> by BuLi addition to $[(OC)_5Cr(^tBu_2PH)]$, with (34) in t.h.f. at low temperature produces the complex $[(OC)_5Cr(\mu\text{-}P^tBu_2)RhCOD]$[121]. Similarly, the reaction of $Li[(OC)_4M(Ph_2PH)(Ph_2P)]$ (M=Cr,Mo,W) with (35) gives a 'bridge-assisted' reaction to generate $[(OC)_4M(\mu\text{-}PPh_2)_2Ir(H)COD]$[122].

Most interestingly, there are several reports of metal complexes containing sulphur ligands bridge-cleaving (34) and (35) to give heterobimetallic systems. These useful 'metal-ligands' include the examples given in Chapter 1, Equation [12] ($[(C_5H_5)_2M(SR)_2]$ (M=Mo,W) (14)[33]); Scheme 5 ($[Mo(C_5H_4(CH_2)_2SR)_2(SR)_2]$ (15)[36,37]); reference (41) ($[Rh_2(\mu\text{-}C_7H_4NS_2)_2(COD)_2]$); and the novel sulphido-bridged bimetallic $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (64)[123], which will be discussed later on in this Chapter.

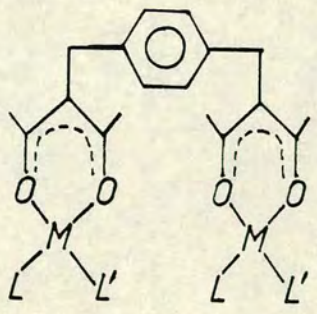
The chemistry of the derivatives of (34) and (35) has been investigated primarily with a view to displacement of the generally labile 1,5-COD fragment. Neutral π-acceptor ligands, such as CO and phosphines appear most reactive.

2.2.2 CHEMISTRY OF THE DERIVATIVES OF $[CODMCl]_2$ (M=Rh(34); M=Ir(35))

If $[CODRh(\mu\text{-}N_3)]_2$ is treated with CO in benzene for several hours $[(OC)_2Rh(\mu\text{-}N_3)]_2$ is generated. However, extended treatment with CO leads to the formation of the well known cluster complex $[Rh_6(CO)_{16}]$[101]. Similarly, reaction of $[CODIr(\mu\text{-}SPh)]_2$ with CO in pentane gives $[(OC)_2Ir(\mu\text{-}SPh)]_2$, which has been characterised by X-ray diffraction[108]. When CO is bubbled through a tetrahydrofuran solution of $[CODIr(\mu\text{-}C_3H_3N_2)]_2$ a light yellow solution is formed. Work-up of the solution leads to decomposition of the product. However if two equivalents of PPh_3 are added after CO treatment, the stable product identified as $[(OC)(PPh_3)Ir(\mu\text{-}C_3H_3N_2)]_2$ (41) can be isolated. If complex (40) is treated with CO in pentane the stable tetracarbonyl complex (42) (L=L'=CO) is produced. This on addition of two equivalents of PPh_3 forms (42) (L=CO; L'=PPh_3), while four equivalents of PPh_3 gives (42) (L=L'=PPh_3).

(41)

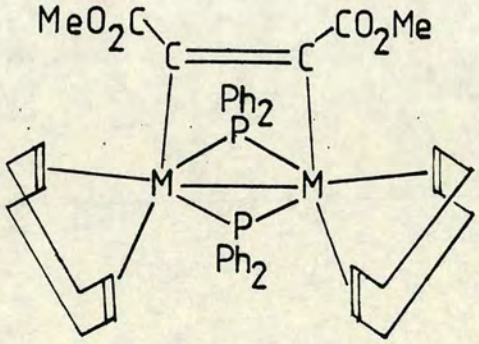
(42)



Addition of an equimolar quantity of diphosphine $PPh_2(CH_2)_nPPh_2$ (n=1-4) to $[CODRh(\mu\text{-}PPh_2)]_2$ (43) generates

$[CODRh(\mu\text{-}PPh_2)_2Rh(\widehat{P\ P})]$, which gives the stable bis(diphosphine-P,P) complex $[(\widehat{P\ P})Rh(\mu\text{-}PPh_2)]_2$ on treatment with further diphosphine ligand[105]. Under ambient conditions reaction of (43) with monodentate phosphines such as PEt_3 gives the mixed ligand complex $[CODRh(\mu\text{-}PPh_2)_2Rh(PEt_3)_2]$ only. Under a hydrogen atmosphere however both 1,5-COD ligands can be replaced to give $[(PEt_3)_2Rh(\mu\text{-}PPh_2)]_2$[106]. $[CODRh(\mu\text{-}PPh_2)]_2$ (43) also undergoes facile binuclear oxidative addition with the electron-poor alkyne $MeO_2CC{\equiv}CCO_2Me$ to give a dimetallated alkene moiety (44). The high-frequency chemical shift of the phosphido groups (δP=176 p.p.m.) implies M-M bond formation. A crystal structure determination for (44) confirms this with an Rh-Rh distance of 2.687Å.[124]

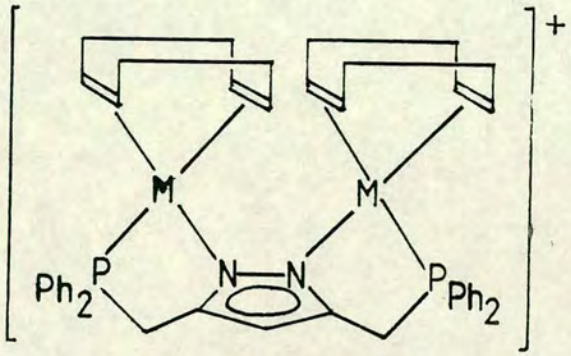
(44)



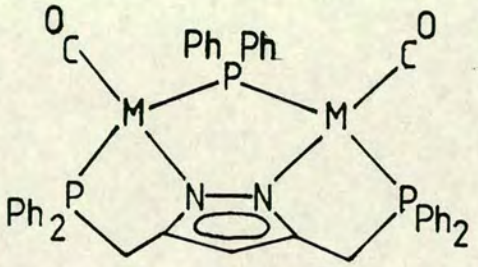
The monomeric complexes $[CODRh(\widehat{S\ S})]$ ($\widehat{S\ S}=S_2P(OPh)_2^-$, $S_2P(C_5H_{11})_2^-$) react with CO in CH_2Cl_2 to give the bis(carbonyl) derivatives $[(OC)_2Rh(\widehat{S\ S})]$. $[CODRh(\widehat{S\ S})]$ also undergo oxidative addition reactions to give stable Rh(III) complexes of the type $[CODRh(\widehat{S\ S})I_2]$[115].

The homobimetallic complex $[COD_2M_2PNNP]BF_4$ (45)

(M=Rh,Ir) demonstrates some interesting modes of reactivity.



(45a, M=Rh; 45b, M=Ir)



(47)

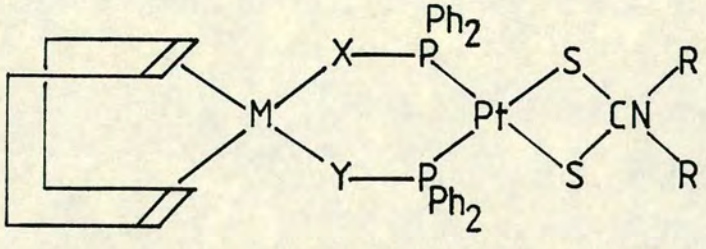
The binucleating PNNP ligand holds both metals in close proximity but at a distance sufficient to exclude M-M bond formation (in contrast to metal 'A-frame' complexes). The tetracarbonyl cation $[(OC)_4M_2PNNP]BF_4$ (46) is produced under mild conditions by passing CO through a CH_2Cl_2 solution of (45). In (46) the high trans-effect of P labilises both 'inner' CO groups, which can be replaced by a variety of anionic groups. Treatment of (46) with Cl^- produces the chlorobridged species $[(OC)_2M_2(\mu\text{-}Cl)PNNP]$, while treatment with $LiPPh_2$ at low temperatures gives the phosphido-bridged complex $[(OC)_2M_2(\mu\text{-}PPh_2)PNNP]$ (47) [125]. At -78°C (45b) oxidatively adds dihydrogen at one Ir(I) centre leaving the other Ir(I) centre deactivated. This mixed-valence complex at -10°C reductively eliminates H_2 regenerating (45b) and this process is reversible. The chloro- and phosphido (47)-bridged compounds undergo an extensive range of oxidative addition reactions with classical electrophiles such as methyl iodide and acetyl-chloride. The bimetallic redox behaviour of the various

systems was rationalised on the basis of the electron-richness of the metal centres as indicated by the ν_{CO} stretching frequency [126].

Finally in this section, prehydrolysed Ph_2PCl, giving an in situ mixture of $Ph_2P(O)H$ and HCl, reacts with $[CODIrCl]_2$ in MeOH to form the Ir(III) 'oxyring' complex $[CODIrHCl(Ph_2PO)_2H]$. The 1,5-COD ligand is readily substituted by bidentate ligands such as dppe, dpae (3) and $NH_2R_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (12) [27,127].

2.3.1 REACTION OF $NH_2R_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (6), $[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)H]$ (7) and $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ (2) with $[CODMCl]_2$ ((34) M=Rh, (35) M=Ir)

$[Pt(S_2CNR_2)(Ph_2PS)_2]^-$, $[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)]^-$ or $[Pt(S_2CNEt_2)(Ph_2PO)_2]^-$ react with $[CODRhCl]_2$ or $[CODIrCl]_2$ in 2:1 molar ratios to produce the dibridged, neutral heterobimetallics (48-55) containing a coordinated 1,5-COD moiety. These complexes have been fully characterised by multinuclear n.m.r. and infra-red spectroscopy, microanalysis and for (48) and (50) by single crystal X-ray diffraction.



(48-55)

	M	X,Y	R		M	X,Y	R
(48)	Rh	S,S	Et	(50)	Ir	S,S	Et
(49)	Rh	S,S	^{i}Pr	(51)	Ir	S,S	^{i}Pr
(52)	Rh	S,O	Et	(53)	Ir	S,O	Et
(54)	Rh	O,O	Et	(55)	Ir	O,O	Et

2.3.2 REACTION OF $NH_2R_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (R=Et,^{i}Pr) WITH $[CODMCl]_2$ (M=Rh,Ir).

Treatment of $[CODRhCl]_2$ (34) with two equivalents of $NH_2Et_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (6) in chloroform solution under ambient conditions is accompanied by a rapid colour change from orange to red. A pale-yellow solid can be precipitated from the reaction solution on addition of methanol. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the recovered product, run in $CDCl_3$ at room temperature, shows a single 1.4.1 triplet of doublets resonance with $\delta P=32.0$ p.p.m. The triplet splitting of 3488.8Hz is consistent with a one-bond $J_{^{195}Pt-^{31}P}$ coupling (^{195}Pt, $I=\frac{1}{2}$, 33.3% abundant) while the smaller splitting of 1.7Hz is consistent with a two-bond $J_{^{103}Rh-^{31}P}$ coupling (^{103}Rh, $I=\frac{1}{2}$, 100% abundant). The single resonance from the quantitative reaction indicates the equivalence of the P atoms in the product and the $^{2}J_{RhP}$ coupling supplies cogent evidence for the formation of the dimetallic six-membered ring

system $\overline{\text{RhSPPtPS}}$.

The high-resolution ^{1}H n.m.r. of the product (Figure 3) shows a quartet ($\delta C\underline{H}_2$ 3.54 p.p.m.) and triplet ($\delta C\underline{H}_3$ 1.12 p.p.m.) resonance for the ethyl groups of the dithiocarbamate ($S_2CNEt_2^-$) ligand and two multiplets ($\delta\underline{H}$ 7-8 p.p.m.) for the protons of the phenyl groups on the bridging phosphorus atoms. Three broad peaks are observed for the coordinated cyclooctadiene. The higher frequency resonance is assigned to the olefinic protons ($\delta C\underline{H}$ 4.0 p.p.m.) and the remaining two signals of equal integral ($\delta C\underline{H}_2$ 2.15, 1.71 p.p.m.) to the two types of aliphatic protons (H_i and H_o in Figure 2). It is clear from the peak integrals that one 1,5-COD moiety is present for each $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ unit. Thus ^{1}H and ^{31}P-{^{1}H} n.m.r. evidence for the yellow product is consistent with the formulation $[CODRh(\mu\text{-}SPPh_2)_2\text{-}Pt(S_2CNEt_2)]$ (48) and the structure shown in Figure 2.

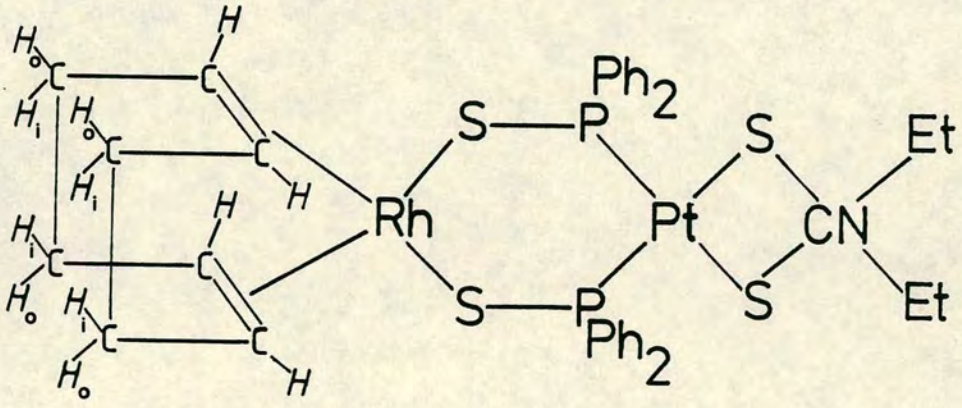
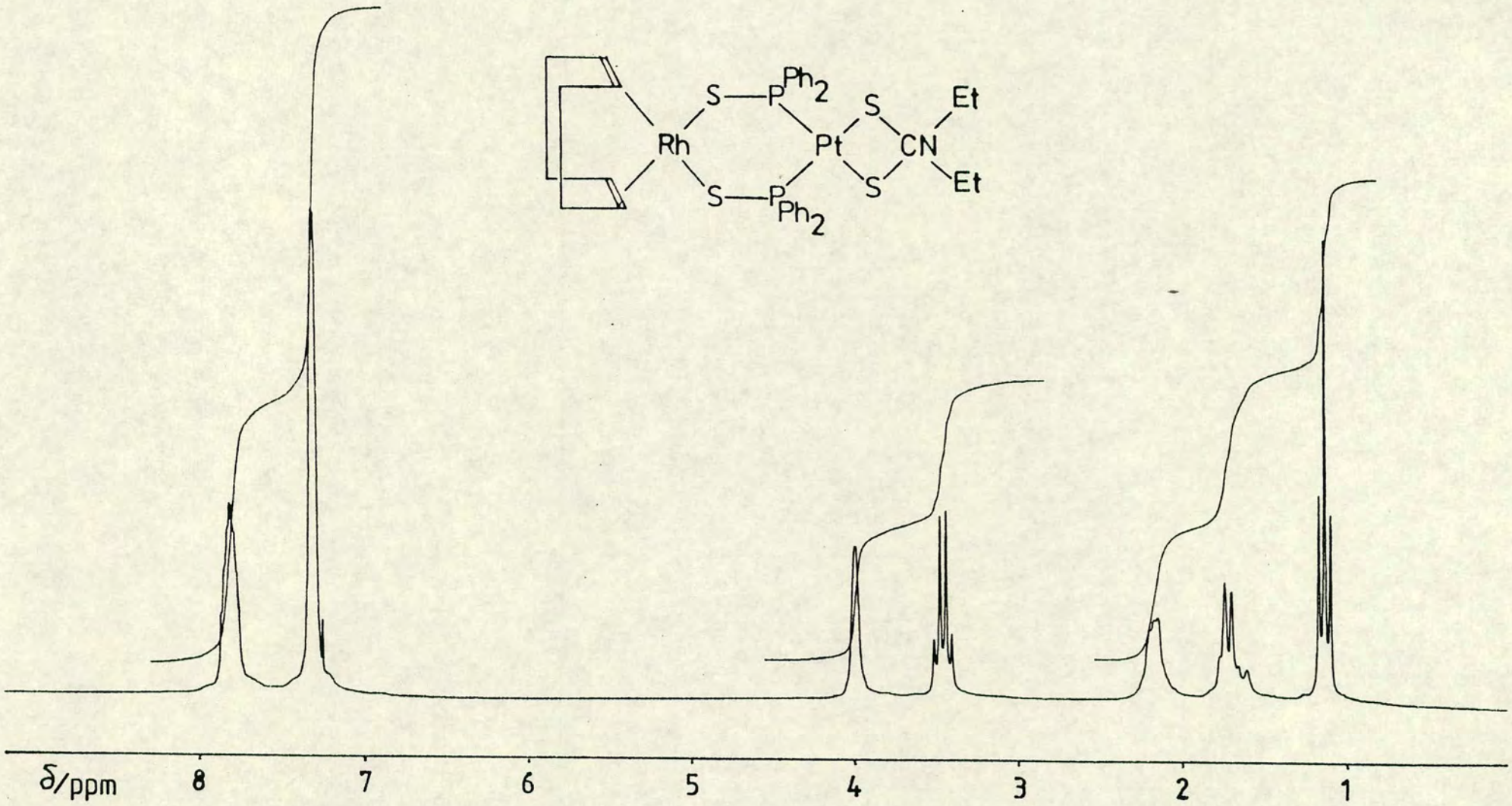


Figure 2:

The structure of (48) showing the three proton types H_o, H_i and H for the coordinated 1,5-COD ligand.

Figure 3: The ^1H n.m.r. spectrum of $[CODRh(SPPh_2)_2Pt(S_2CNEt_2)]$ (48) in $CDCl_3$ at 298°K.

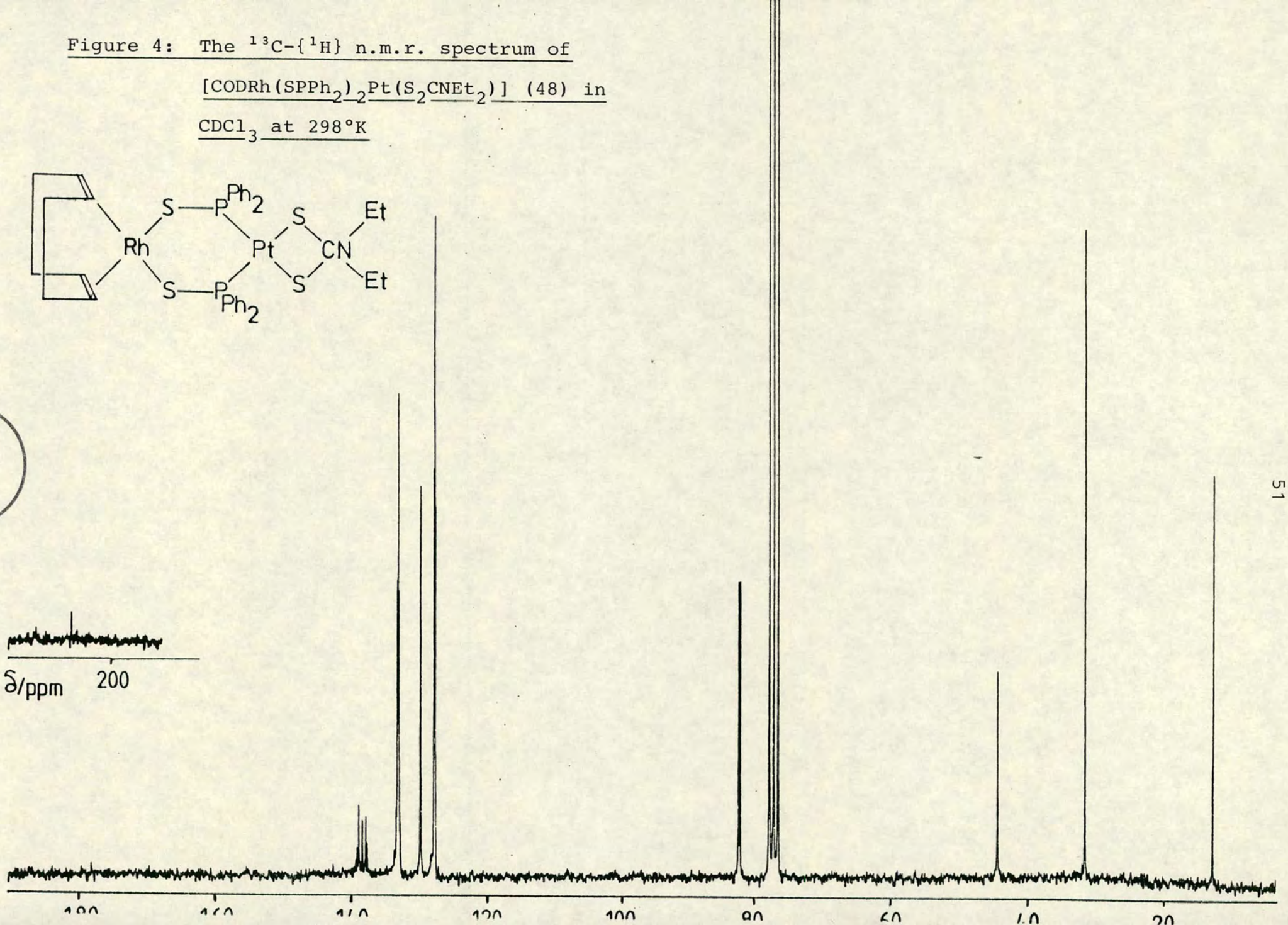


The $^{13}C-\{^{1}H\}$ n.m.r. spectrum of (48) (Figure 4) shows five non-phenyl carbon environments as required for the proposed structure. The resonances at δ_C 43.9, 12.2 and 205.8 p.p.m. can be assigned to $\delta\underline{C}H_2$, $\delta\underline{C}H_3$ and $\delta\underline{C}N$ respectively for the dithiocarbamate ligand. For the 1,5-COD ligand two resonances appear. The peak at 81.9 p.p.m. showing a $^{1}J_{RhC}$ coupling of 11.6Hz is assigned to the four olefinic carbons ($\delta\underline{C}H$) and the remaining singlet at 30.9 p.p.m. to the four equivalent methylene carbons ($\delta\underline{C}H_2$). The phenyl carbon signals appear in the region 127-140 p.p.m.

Two strong bands can readily be identified in the i.r. spectrum of (48). In complexes containing the dithiocarbamate ligand ν_{CN} is generally found in the region 1540-1480 cm^{-1} [128] and in this case is detected at 1512 cm^{-1}. It is also known that the ν_{PS} stretch in bridging phosphine-sulphide metal complexes falls in the region 600-575 cm^{-1} [5] and for (48) is found at 595 cm^{-1}. Various other bands can be attributed to the dithiocarbamate and 1,5-COD ligands. A mass spectrum of (48), obtained by Fast Atom Bombardment ionisation (FAB), gave the required $(M+H)^+$ parent ion peak at 990 m/e, with the first fragmentation peak at 882 m/e corresponding to the loss of 1,5-COD (-108 m/e) from the parent. C,H,N microanalysis results support the proposed formulation and the non-electrolytic behaviour in CH_2Cl_2 or acetone confirms the non-ionic nature of (48).

Compounds (49-51) were prepared following the procedure used to prepare (48) using the appropriate combination of substrates $NH_2R_2[Pt(S_2CNR_2)(Ph_2PS)_2]$ (R=Et, ^{i}Pr) and $[CODMCl]_2$ (M=Rh,Ir). Some empirical observations result

Figure 4: The $^{13}C-\{^{1}H\}$ n.m.r. spectrum of $[CODRh(SPPh_2)_2Pt(S_2CNEt_2)]$ (48) in $CDCl_3$ at 298°K



from the characterisation of the S,S-bridged heterobimetallics (48-51). For a given compound a change in the alkyl group from Et to ^{i}Pr for the dithiocarbamate ligand results in an up-frequency shift in δP and a reduction in the $^{1}J_{PtP}$ coupling constant of between 15-60Hz. This change is also reflected in the ν_{CN} stretching frequency, which is shifted to lower energy by about 20 cm^{-1}. A change in metal from Rh to Ir ((48) c.f. (50) or (49) c.f. (51)) removes the doublet metal coupling from the various n.m.r. spectra. This also provokes a down-frequency shift in $\delta_{C}\underline{C}H$ and $\delta_{H}C\underline{H}$ for the 1,5-COD ligand, which is in line with moving from the 2nd to 3rd row metal.[129]

$[CODRh(\mu\text{-}SPPh_2)_2Pt(S_2CNR_2)]$ ((48) R=Et, (49) R=^{i}Pr) can also be synthesised by the rapid, equimolar reaction of (6) and $[CODRh(PPh_3)_2]BPh_4$. The $^{31}P\text{-}\{^{1}H\}$ n.m.r. spectrum of the $CDCl_3$ reaction solution reveals that both PPh_3 ligands are liberated (δP= -6 p.p.m., Free PPh_3) with the formation of the heterobimetallic ((48), δP 32.0, $^{1}J_{PtP}$=3488.8Hz, $^{2}J_{RhP}$=1.7Hz). [Equation 31]

$$NH_2R_2[Pt(S_2CNR_2)(PPh_2S)_2] + \tfrac{1}{2}[CODRhCl]_2$$

$$\downarrow \; CDCl_3 \;|\; -NH_2R_2Cl$$

$$[CODRh(\mu\text{-}SPPh_2)_2Pt(S_2CNR_2)] \quad (48),(49)$$

$$\uparrow \; CDCl_3 \;|\; -2PPh_3$$

$$NH_2R_2[Pt(S_2CNR_2)(PPh_2S)_2] + [CODRh(PPh_3)_2]BPh_4$$

--------[31]

Single crystals of suitable quality for X-ray studies were grown for $[CODRh(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]$ (48) and $[CODIr(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]$ (51). Some crystal data, bond lengths and angles are provided in the experimental section. The structure of (48) is illustrated in Figure 5. It shows both metals in planar environments linked by two Ph_2SP^- units forming a six-membered, dimetallated ring $\overline{RhSPPtPS}$. The platinum retains the dithiocarbamate chelate with trans-positions occupied by phosphorus. The rhodium coordination is satisfied by two sulphur atoms and a η^4-cyclooctadiene ligand. The P-S bond length increases from 1.99(1)Å in the anion (6)[26] to 2.049(5) in (48) consistent with a decrease in bond order and is comparable with the P-S bond length observed in similar systems ($[Pt(S_2CNEt_2)(\mu\text{-}Ph_2PS)_2Pt(S_2CNEt_2)]$, 2.040(5)Å [5]; $M[N(PR_2S)_2]_2$; M=Ni, 2.023(6)Å [130]; M=Fe, 2.020(8)Å [131]). A pseudo-boat conformation best describes the arrangement of the six-membered, heavy-atom ring (Figure 6) with a metal-metal through-space distance of 4.351(1)Å. This ring conformation is also adopted in $[Pt(S_2CN^iPr_2)(\mu\text{-}Ph_2PS)_2\text{-}Pt(S_2CNEt_2)]$[5] and $[\{(C_5H_5)Ni(P(OMe)_2S)_2\}_2Ni]$.[31†] A comparison of the structures of (6) and (48) suggests that the S,S-platinum chelate "stretches out" to accommodate the second metal. This is reflected by a drop in the S(1)-S(2) non-bonded distance (4.7 to 3.46Å), a reduction in the

† Conformation of $\overline{NiPSNiSP}$ rings found to be "between a twist-boat and boat form"

P(1)-$\hat{P}$t-P(2) angle (98.6(4) to 93.3(1)°) and an expansion in both Pt-$\hat{P}$-S angles (111.6(6), 117.3(9) to 117.4(2), 122.9(2)°).

The X-ray structure for (51) (Figure 7) is very similar to that of (48). The heavy-atom core retains a pseudo-boat conformation (Figure 8) of slightly greater depth which results in a closer Metal-Metal, through-space distance of 4.273(1)Å.

Interestingly, in both (48) and (51) there is a marked difference in the bridging sulphur to metal distances ((48), Rh-S 2.328(4) and 2.370(4)Å; (51), Ir-S 2.315(4) and 2.379(4)Å). It is unlikely that a crystal packing effect is responsible for this difference as the nearest inter-molecular contact is over 6.7Å in (48) and 6.87Å in (51).

Compounds (48-51) are high-melting, yellow/orange, air-stable solids produced in excess of 80% yield. They are soluble and stable in chlorinated hydrocarbons, toluene and acetone and insoluble in alcohols and ethers.

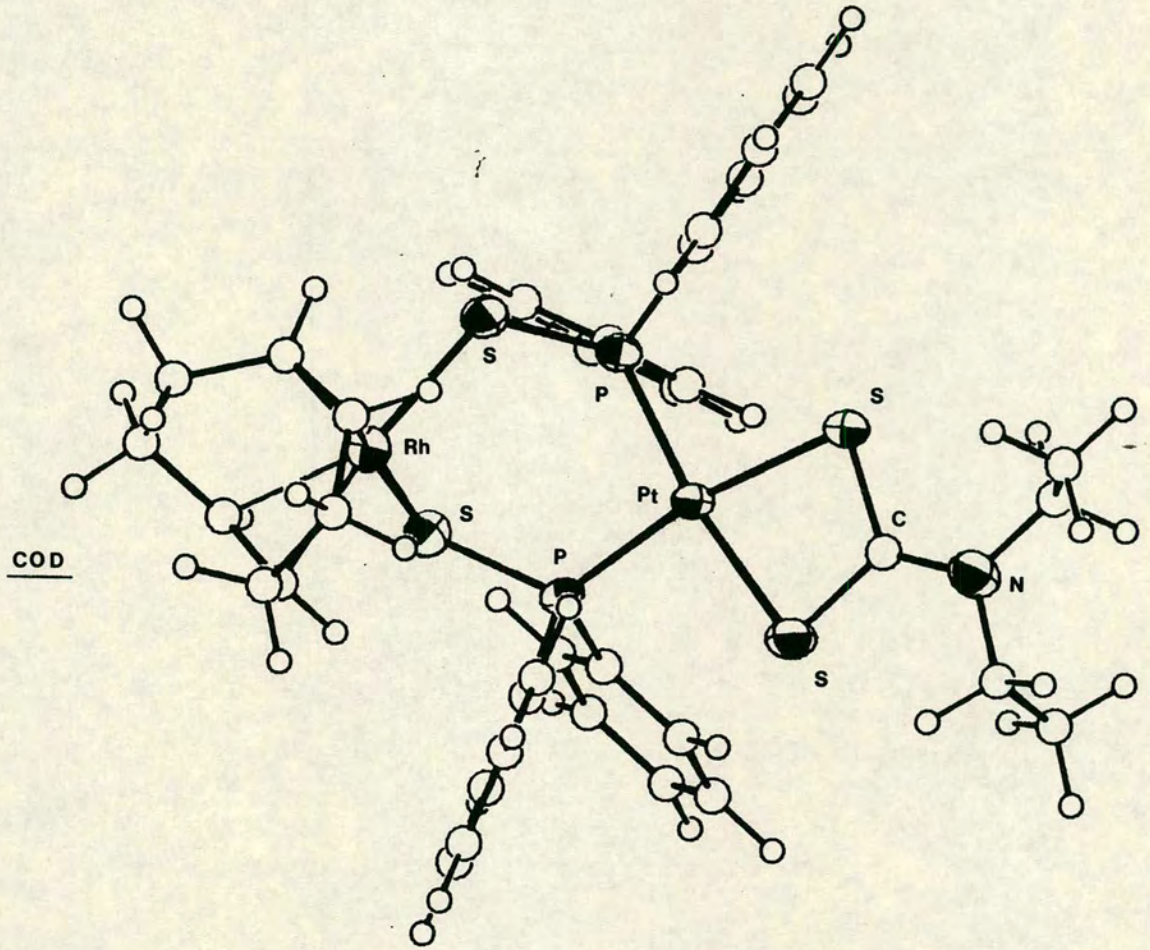


Figure 5: The molecular structure of $[CODRh(SPPh_2)_2Pt(S_2CNEt_2)]$ (48)

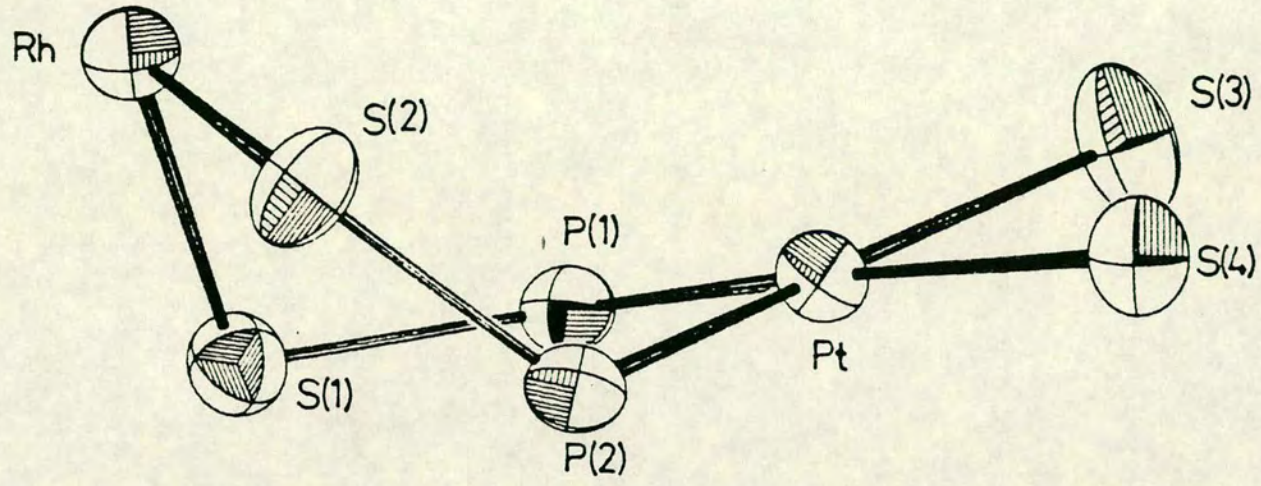


Figure 6: Conformation of heavy-atom core in [CODRh(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (48)

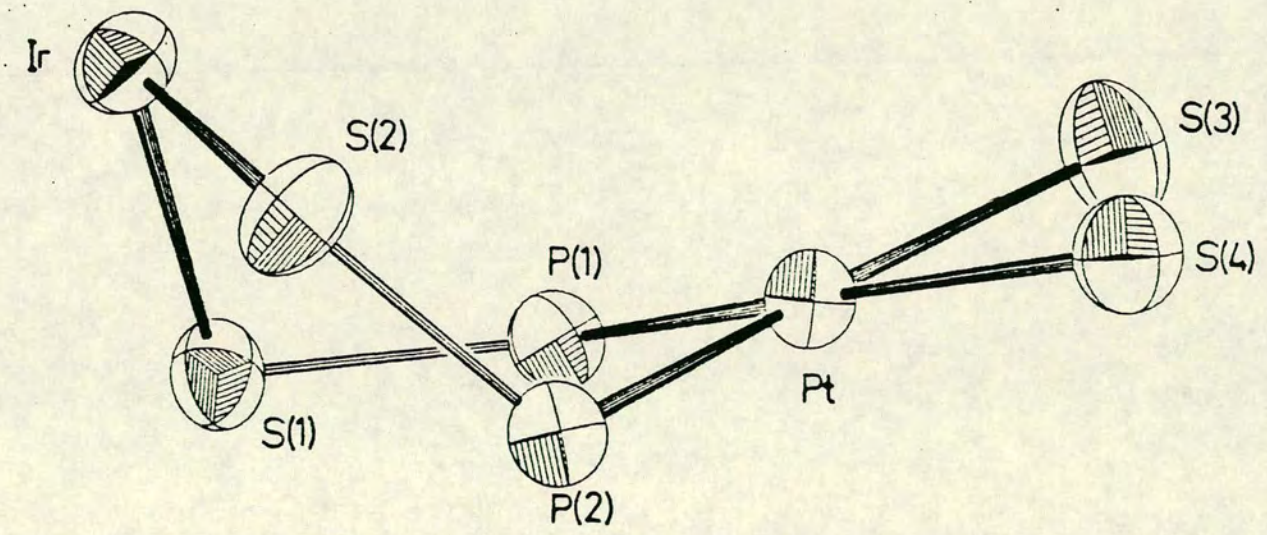


Figure 8: Conformation of heavy-atom core in [CODIr(SPPh$_2$)$_2$Pt(S$_2$CN^{i}Pr$_2$)] (51)

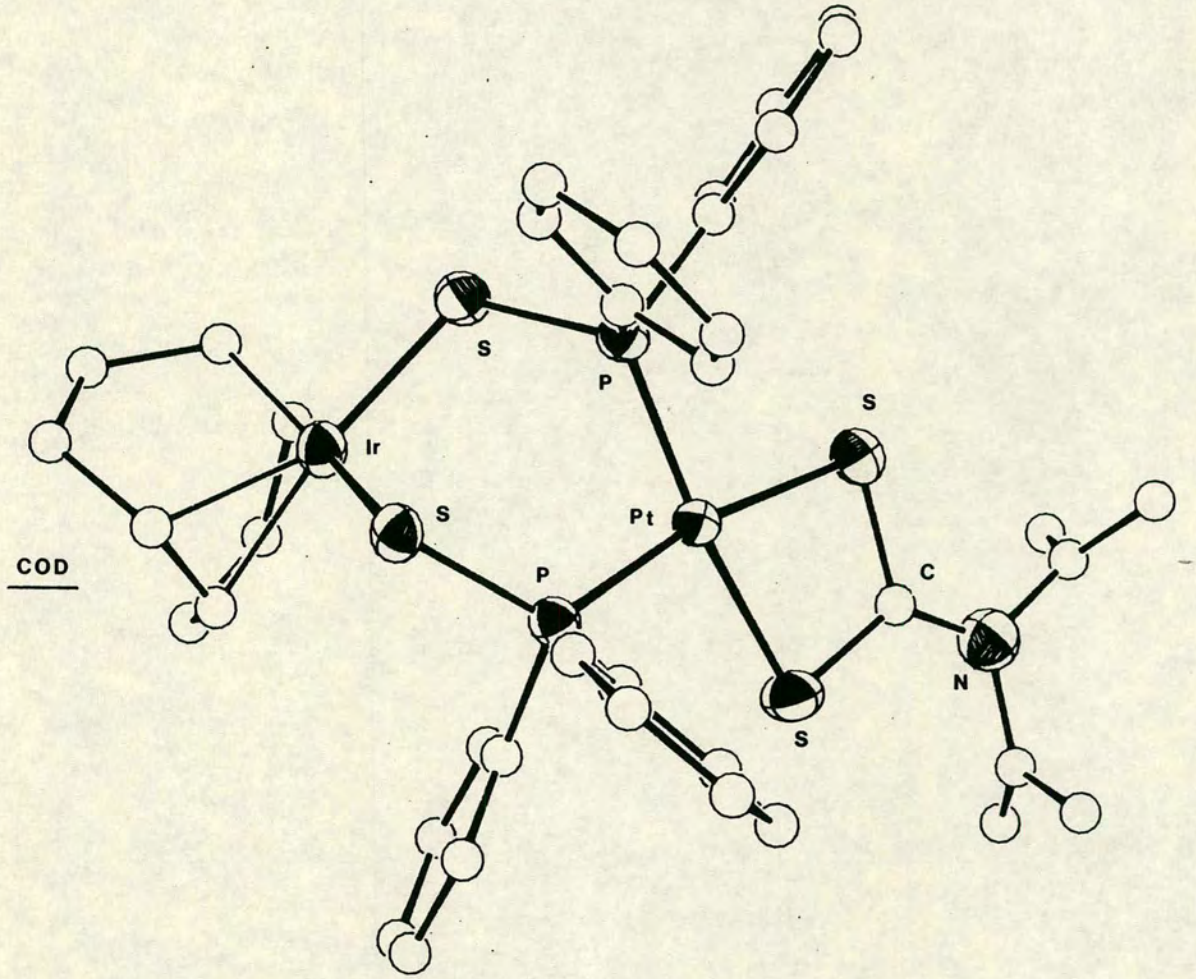
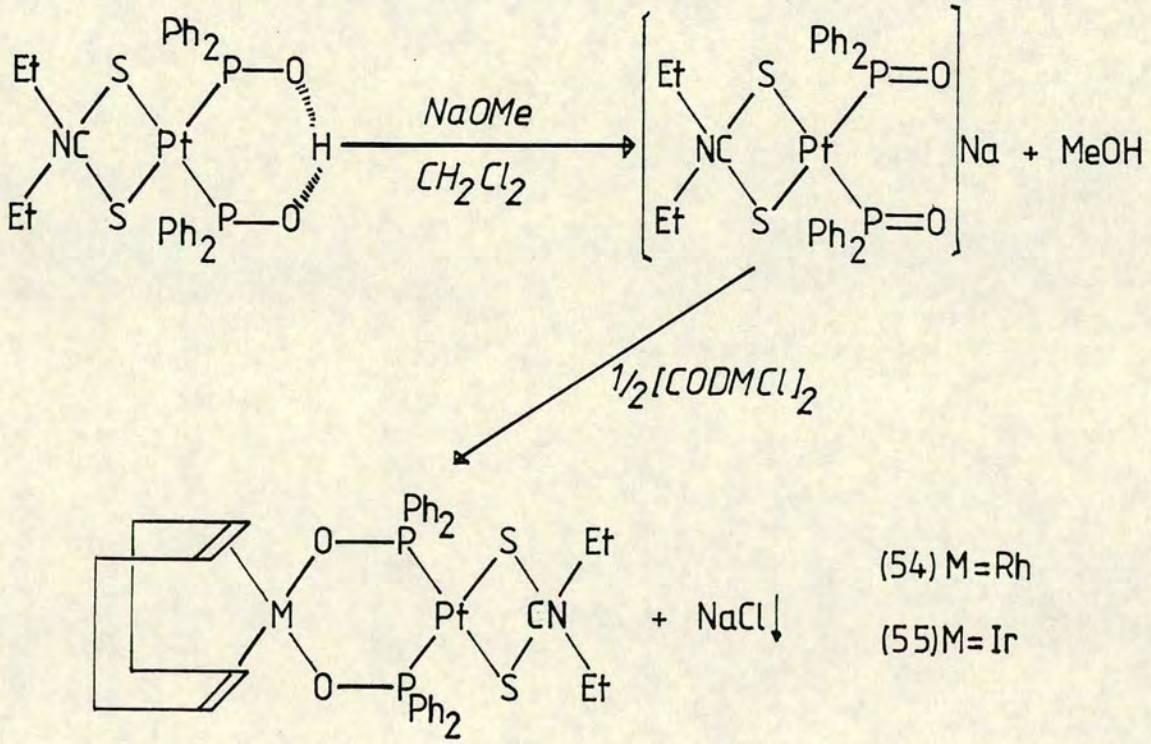


Figure 7: The molecular structure of $[CODIr(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (51)

(H atoms not shown)

2.3.3 THE REACTION OF $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ with $[CODMCl]_2$ (M=Rh,Ir)

No reaction occurs if $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ (2) and $[CODMCl]_2$ are mixed at room temperature or refluxed in various solvents. It is first necessary to remove the acidic ring proton from (2) to generate the anion [Equation 4] before a reaction will proceed. $[Pt(S_2CNEt_2)(Ph_2PO)_2]^-$ is generated *in situ* by the addition of two equivalents of NaOMe to a CH_2Cl_2 solution of (2). Addition of 0.5 molar equivalents of $[CODMCl]_2$ results in an immediate reaction to give a yellow solution. After 10 minutes stirring the NaCl formed during the reaction can be filtered off and a lemon coloured solid recovered by addition of methanol to the filtrate. Spectroscopic and analytical evidence suggests the formulation of the products as the neutral O,O-bridged heterobimetallics $[CODRh(\mu\text{-}OPPh_2)_2Pt(S_2CNEt_2)]$ (54) and $[CODIr(\mu\text{-}OPPh_2)_2Pt(S_2CNEt_2)]$ (55) [Equation 32].

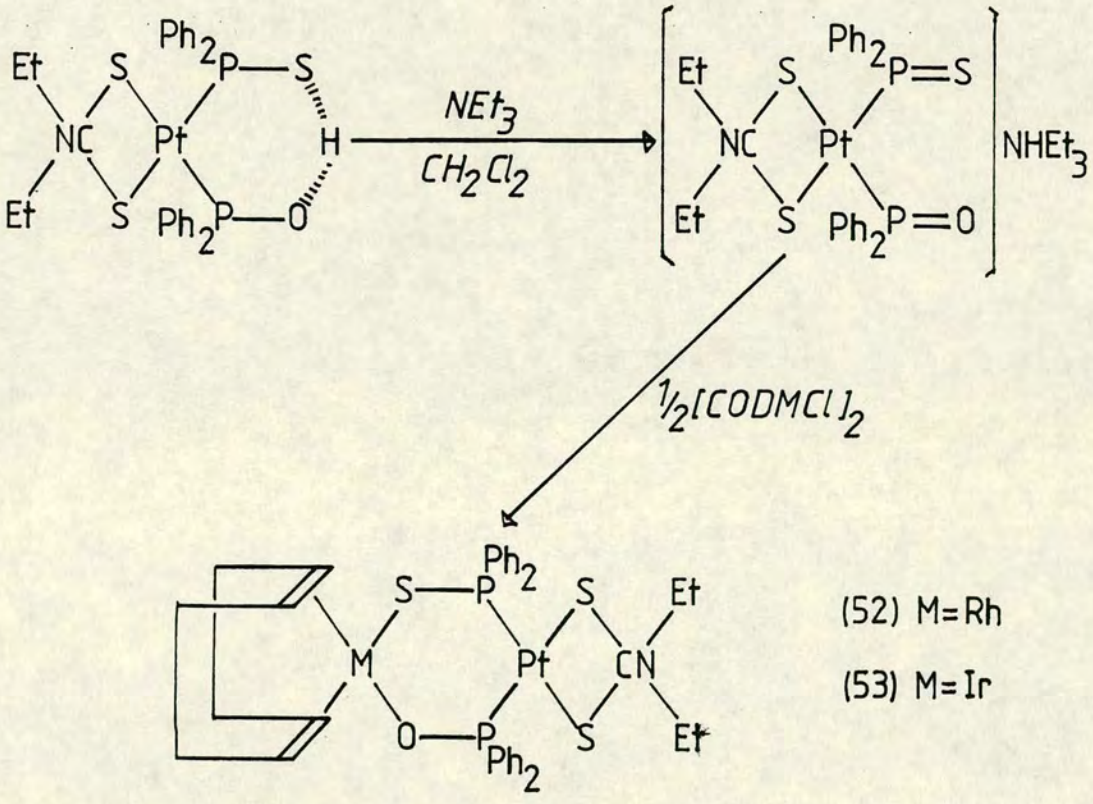


--------[32]

The n.m.r. and i.r. spectra for (54) and (55) take the same form as their S,S-bridged analogues (48) and (50) respectively, with the change in group 6 bridging atom causing shifts of varying magnitude in the observed signal position for comparable moieties.

2.3.4 REACTION OF $[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)H]$ with $[CODMCl]_2$ (M=Rh,Ir)

As required in the previous section for $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$, the acidic ring proton of $[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)H]$ (7) must be removed by treatment with suitable base to generate the anion before reaction with $[CODMCl]_2$ proceeds to yield the yellow (52) or brown (53) mixed S,O-bridged heterobimetallics [Equation 33].



(52) M=Rh

(53) M=Ir

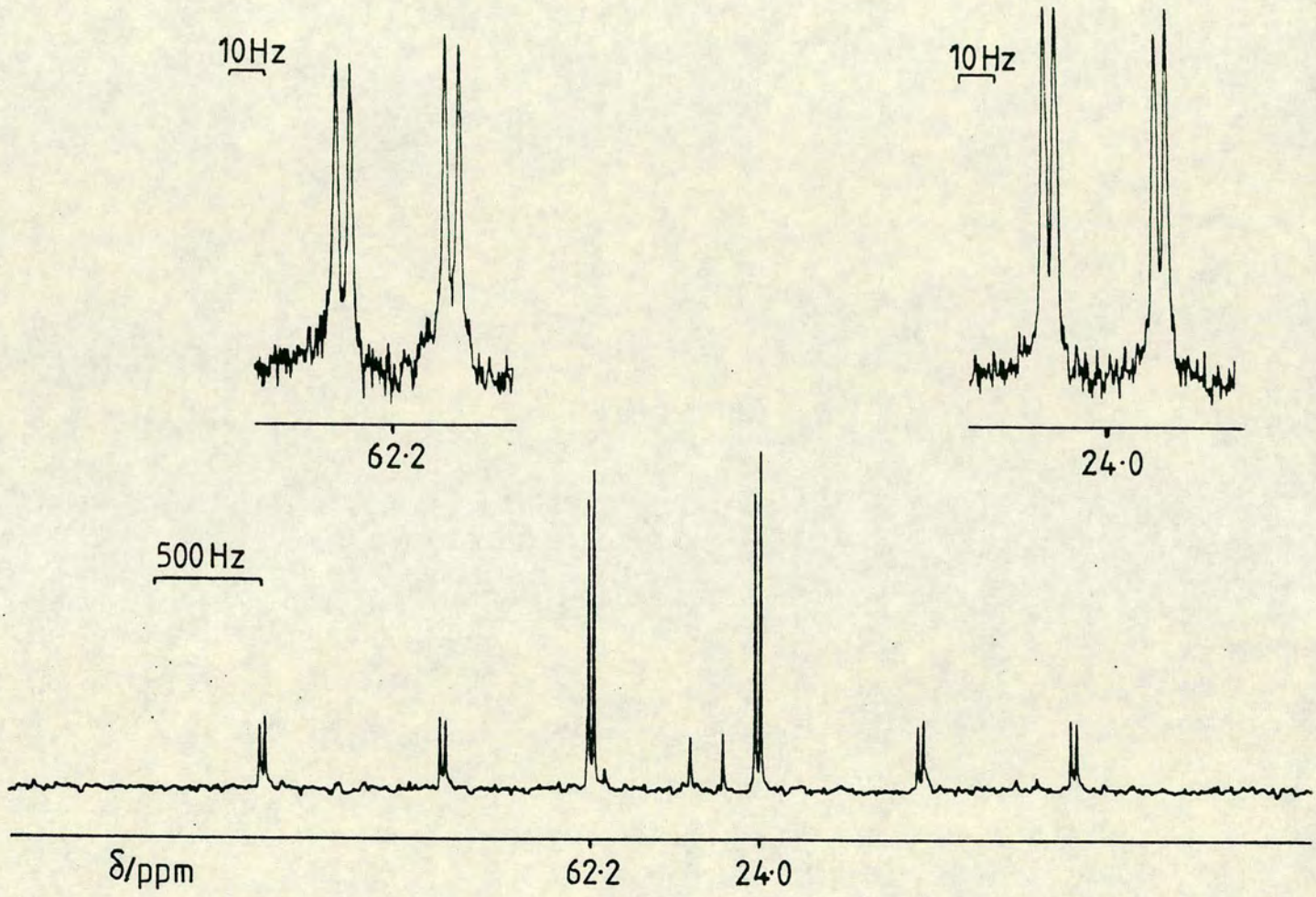
----------[33]

As a consequence of mixed S,O-bridging with subsequent reduction in molecular symmetry, the $^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$ n.m.r. spectra for (52) and (53) are more complex than those obtained for the related S,S- and O,O-bridged heterobimetallics.

The $^{31}P-\{^1H\}$ n.m.r. spectrum of $[CODRh(\mu\text{-}SPPh_2)(\mu\text{-}OPPh_2)Pt(S_2CNEt_2)]$ (52) shown in Figure 9 consists of two (δP_O 62.2, δP_S 24.0 p.p.m.) 1.4.1 triplet ($^1J_{PtP_O}$ 3647.5, $^1J_{PtP_S}$ 3496.1Hz) of doublet ($^2J_{P_SP_O}$ 30.3Hz) resonances, which on closer inspection reveal further doublet splittings ($^2J_{RhP_O}$ 3.9, $^2J_{RhP_S}$ 3.0Hz) (Figure 9 inserts). The spectrum is consistent with the formation of the six-membered ring system $\overline{RhSPPtPO}$ in which the phosphorus atoms are magnetically inequivalent cis-bound to platinum and two bonds removed from rhodium.

The ^1H n.m.r. for (52) (Figure 10) shows a doubling-up effect for each resonance. The inequivalent ethyl groups appear as a quintet and quartet arising from overlapping quartet ($\delta C\underline{H}_2$) and triplet ($\delta C\underline{H}_3$) resonances respectively. Two olefinic resonances appear, as in (38)[117], for the coordinated 1,5-COD ligand. The higher-frequency signal ($\delta C\underline{H}$ 3.80 p.p.m.) is assigned to the protons of double bond trans to S and the lower-frequency signal to the protons of the double bond trans to O based on a comparison of the δCH values found for (48) and (54) (δCH 3.98 and 3.66 p.p.m. respectively). The methylene protons of the 1,5-COD ligand are remarkably well resolved into two sets of two resonances. In the symmetrical S,S- and O,O-bridged systems there is 'inbuilt' inequivalence in the coordinated

Figure 9: The $^{13}P-\{^{1}H\}$ n.m.r. spectrum of $[CODRh(SPPh_2)(OPPh_2)Pt(S_2CNEt_2)]$ (52) in $CDCl_3$ at 298°K



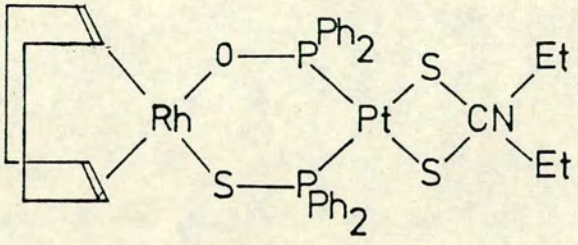
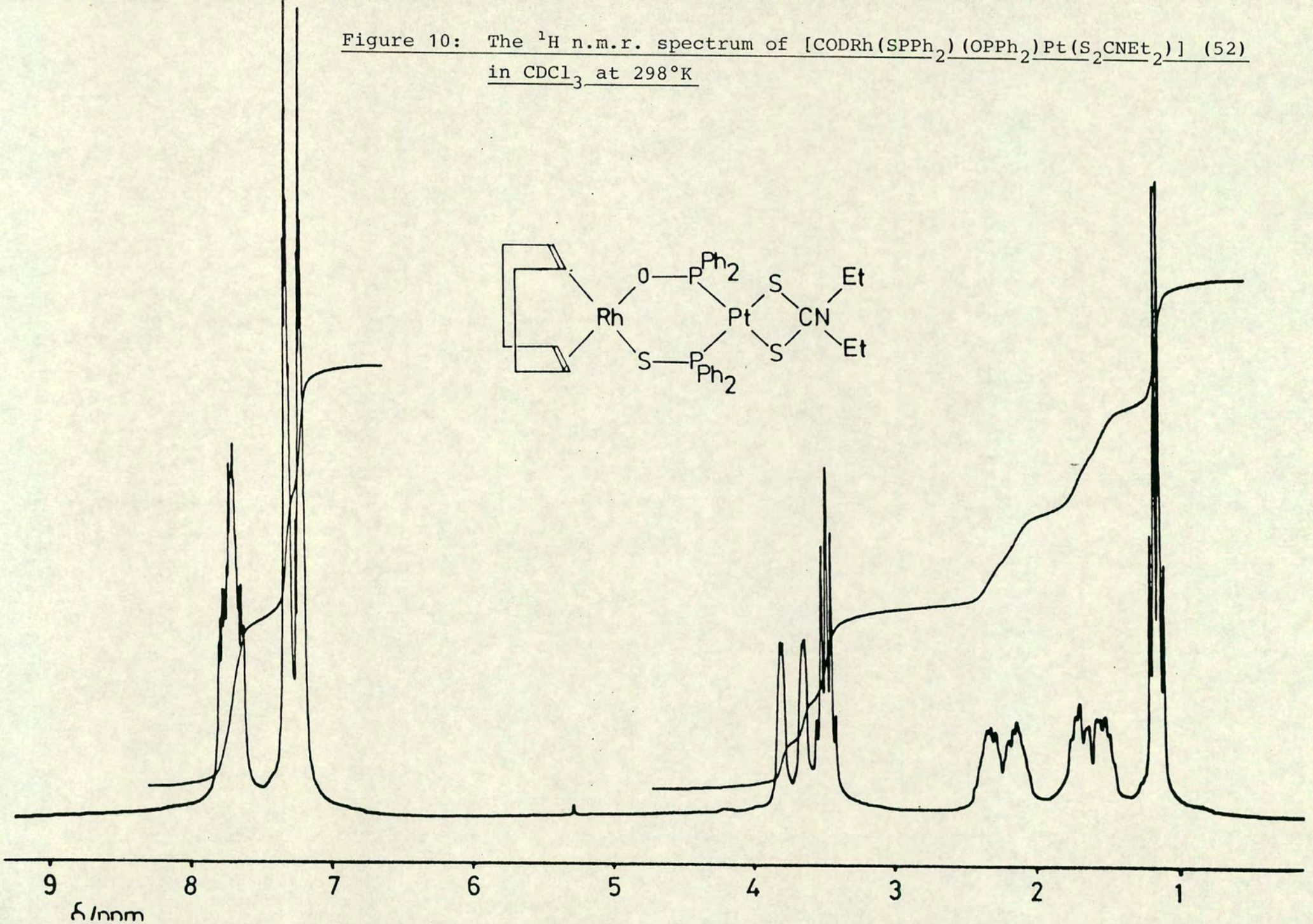


Figure 10: The ^1H n.m.r. spectrum of $[CODRh(SPPh_2)(OPPh_2)Pt(S_2CNEt_2)]$ (52) in $CDCl_3$ at 298°K



1,5-COD ligand (H_o, H_i in Figure 2). An additional feature in this case is that two groups are <u>trans</u> to S and two <u>trans</u> to O. Thus, four methylene proton environments result with two protons per environment (Figure 12). The resonance integrals are correct for one 1,5-COD ligand and one $[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)]^-$ unit.

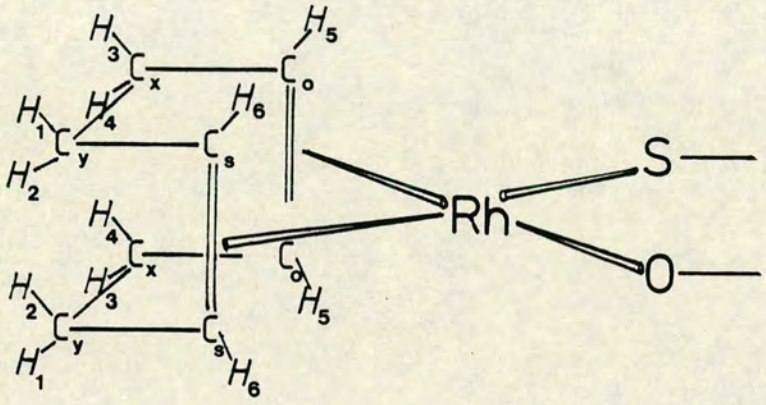
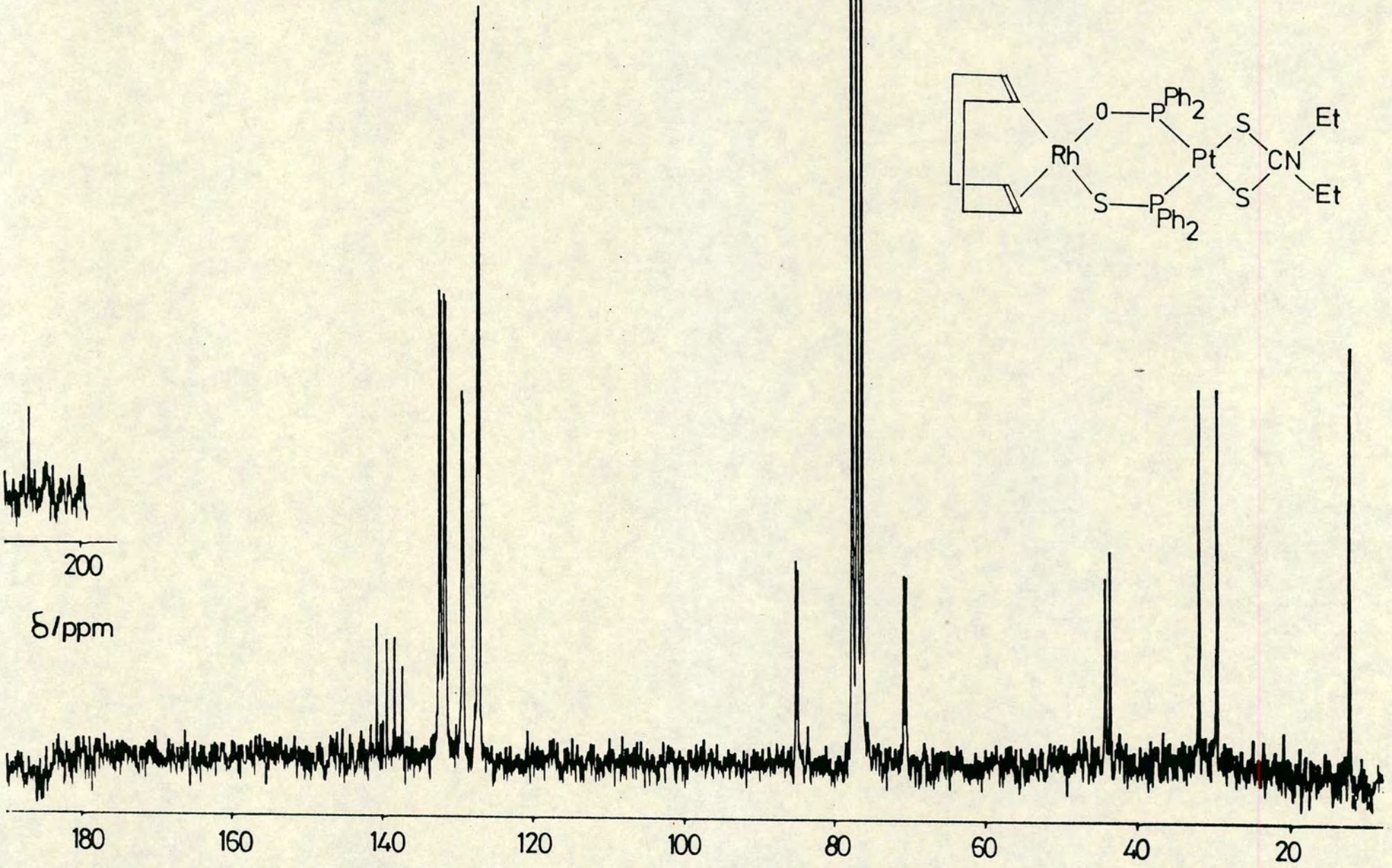


Figure 12: The proton (H_1-H_6) and carbon (C_o,C_s,C_x,C_y) environments for the 1,5-COD ligand in (52)

The ^{13}C-{^1H} n.m.r. spectrum for (52) is shown in Figure 11. Two olefinic carbon ($\delta_{\underline{C}H}$ <u>trans</u> to S 84.5, $^1J_{RhC}$ 11.6; $\delta_{\underline{C}H}$ <u>trans</u> to O 70.6 p.p.m., $^1J_{RhC}$ 14.1Hz) and two methylene carbon ($\delta_{Cx,Cy}$ 31.9, 29.5 p.p.m.) resonances appear for the 1,5-COD ligand as expected for the structure depicted in Figure 12. The methylene carbons of the two ethyl groups are in sufficiently different environments for separate resonances ($\delta_{\underline{C}H_2}$ 44.3, 43.6 p.p.m.) to be observed, however a single peak ($\delta_{\underline{C}H_3}$ 12.2 p.p.m.) results for the methyl carbons. The remaining non-phenyl resonance ($\delta_{\underline{C}N}$ 206.7 p.p.m.) of low intensity accounts for the quaternary carbon of the dithiocarbamate ligand.

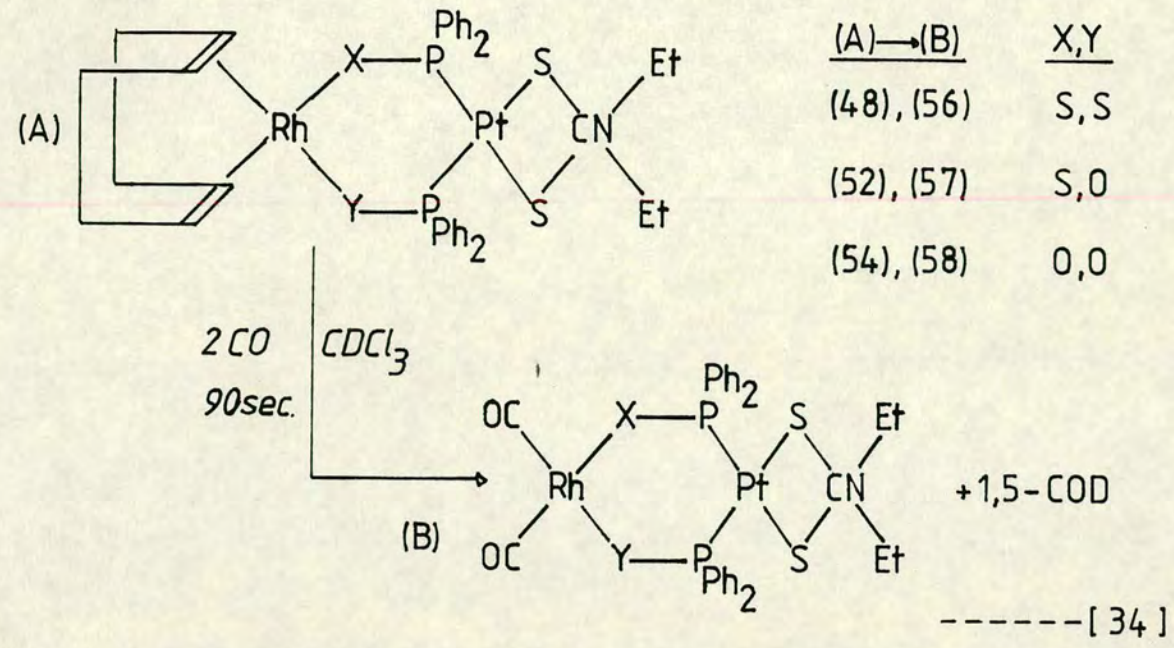
Figure 11: The $^{13}C-\{^{1}H\}$ n.m.r. spectrum of $[CODRh(SPPh_2)(OPPh_2)Pt(S_2CNEt_2)]$ (52) in $CDCl_3$ at 298°K



The i.r. spectrum of (52) shows bands for ν_{PO} (1020 cm^{-1}) and ν_{PS} (582 cm^{-1}) and, with favourable microanalysis results and non-electrolytic behaviour, all available evidence supports the proposed mixed S,O-bridged formulation (52).

2.4 REACTION OF [CODM(XPPh$_2$)(YPPh$_2$)Pt(S$_2$CNEt$_2$)] (M=Rh, (48) X,Y=S,S; (52) X,Y=S,O; (54) X,Y=O,O; M=Ir (55) X,Y=O,O) WITH CO

When CO is bubbled through a $CDCl_3$ solution of (48), (52) or (54) for 90 seconds there is a slight lightening of the yellow solution. The ^1H n.m.r. spectrum confirms that the 1,5-COD ligand is no longer coordinated, with signals for the free ligand appearing at δ_{CH} 5.5 p.p.m. and δ_{CH_2} 2.3 p.p.m. The $^{31}P-\{^1H\}$ n.m.r. spectrum shows changes in δP, but $^1J_{PtP}$ and $^2J_{RhP}$ remain resolved indicating no breakdown of the bimetallic unit. A pale yellow solid can be recovered on addition of Et_2O or MeOH to the reaction solution. The KBr disc or solution i.r. spectra of the products confirm that CO is incorporated. Two carbonyl bands are observed in the region 2100-1950 cm^{-1} typical of the symmetric and asymmetric stretch from a $M(CO)_2$, cis-carbonyl arrangement[132]. Thus all available evidence ($^{31}P-\{^1H\}$, ^1H n.m.r. and i.r. spectroscopy, microanalysis) suggests that CO has substituted for the 1,5-COD ligand to give the bis(carbonyl) derivatives (56-58) [Equation 34].



(A)⟶(B)	X,Y
(48), (56)	S,S
(52), (57)	S,O
(54), (58)	O,O

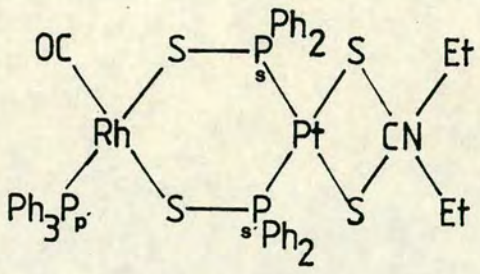
------[34]

Bubbling CO through a $CDCl_3$ solution of $[CODIr(OPPh_2)_2Pt(S_2CNEt_2)]$ (55) produces a colour change orange to ink blue. Based on $^{31}P-\{^1H\}$ n.m.r. and solution i.r. (ν_{CO} 2060, 1984 cm^{-1}) data it is anticipated that the bis(carbonyl) derivative $[(OC)_2Ir(\mu-OPPh_2)_2-Pt(S_2CNEt_2)]$ (59) is formed but isolation of the analytically pure product was unsuccessful.

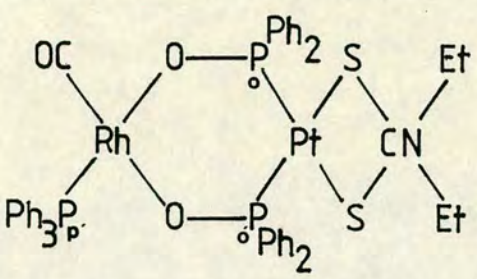
2.5 REACTION OF $[(OC)_2Rh(XPPh_2)(YPPh_2)Pt(S_2CNEt_2)]$ ((56) X,Y=S,S; (57) X,Y=S,O; (58) X,Y=O,O) WITH PPh_3

Addition of an equimolar quantity of PPh_3 to a $CDCl_3$ solution of (56), (57) or (58) results in a vigorous evolution of gas (presumably CO) giving products which are formulated as the mono(carbonyl/phosphine) derivatives $[(OC)(Ph_3P)Rh(XPPh_2)(YPPh_2)Pt(S_2CNEt_2)]$ ((60) X,Y=S,S; (61) X,Y=S,O; (62) X,Y=O,O).

The substitution of CO by PPh_3 in the S,S- and O,O-bridged complexes (56) and (58) gives rise to the products (60) and (62) respectively.



(60)

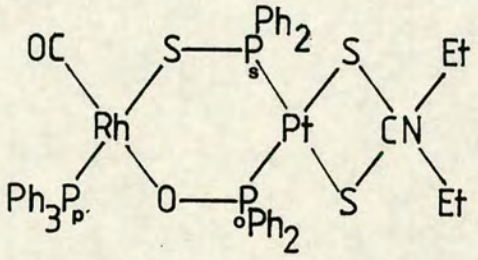


(62)

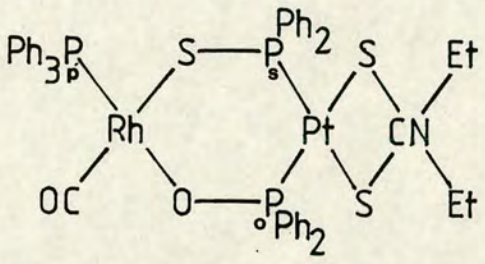
The loss of the plane of symmetry in complexes (60) and (62) is reflected in the $^{31}P-\{^1H\}$ n.m.r. spectra of the complexes. In (62) an AB pattern centred at 58.8 p.p.m. with associated ^{195}Pt satellites appears for δP_o and $\delta P_{o'}$. The rhodium-bound phosphine signal appears at $\delta P_{p'}$, 48.7 p.p.m. with $^1J_{RhP}$ 183.0Hz. When the spectrum is obtained over a narrow spectral width no $^3J_{p'p}$ is detected. The low frequency side of the AB pattern however reveals a further doublet splitting of 2.0Hz resulting from $^2J_{RhP}$ coupling to either P_o or $P_{o'}$ with the remaining coupling equal to or approaching zero. The $^{31}P-\{^1H\}$ n.m.r. spectrum of (60) is that of a first-order ABX (A=P_s, B=$P_{s'}$, X=$P_{p'}$) with additional couplings to the n.m.r. active metal nuclei. The signal for the rhodium-bound phosphine is at $\delta P_{p'}$, 39.6 p.p.m. with $^1J_{RhP}$ 159.4Hz. In this case, $^3J_{P'P_s}$ and $^3J_{p'p_{s'}}$ are detected but their assignment to 17.5 and 8.4Hz remains uncertain. As in (60), $^2J_{RhP}$ can be detected on the low-frequency side of the AB part of the central resonance. The products (60) and (62) can be recovered as

light brown solids on addition of pentane or Et_2O to the golden yellow reaction solutions. A single ν_{CO} peak is detected in the i.r. spectrum of each complex ((60) ν_{CO} 1972 cm^{-1}; (62) ν_{CO} 1970 cm^{-1}).

In the mixed S,O-bridged system (57), displacement of CO by PPh_3 may result in the formation of two products in which the Ph_3P is either trans to S (61a) or trans to O (61b).



(61a)

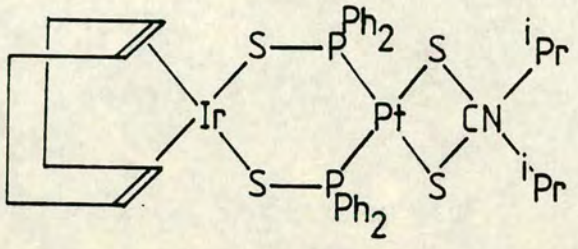


(61b)

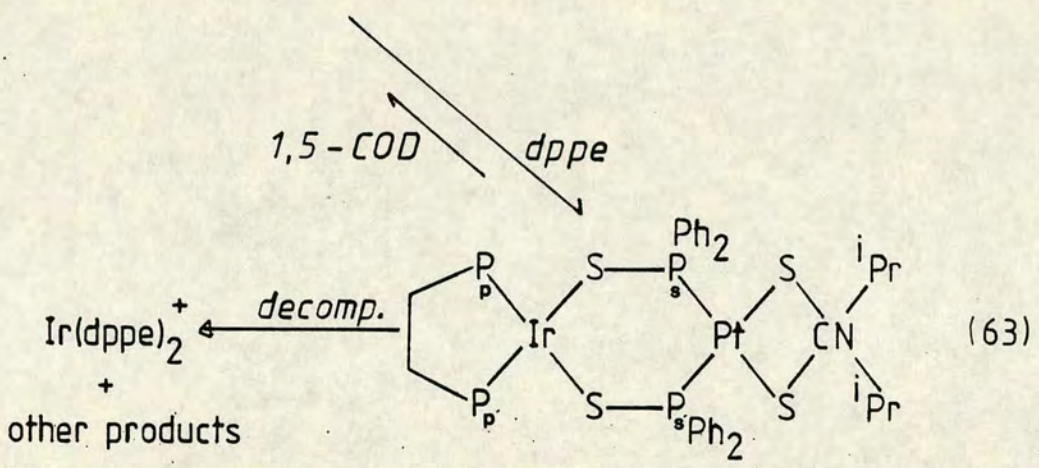
It is clear from the $^{31}P-\{^1H\}$ n.m.r. spectrum of (61) that only one of the possible products is formed. The signals for the bridging phosphorus appear with platinum satellites at δP_o 58.0 p.p.m. and δP_s 25.6 p.p.m. with $^2J_{P_sP_o}$ 31.7Hz. The Rh bound phosphine resonance appears at $\delta P_{p'}$ 35.6 p.p.m. with $^1J_{RhP}$ 166.0Hz. In this case $^2J_{RhP}$ coupling is observed for both δP_s (3.7Hz) and δP_o (3.7Hz) but only $^3J_{p'p_s}$ (6.1Hz) is detected with no measured coupling between $P_{p'}$ and P_o. The i.r. spectrum of the recovered product shows a single ν_{CO} band at 1958 cm^{-1}. A comparison of n.m.r. (especially $^1J_{RhP'}$ and $^3J_{pp'}$) and i.r. (ν_{CO}) data for (61) and (60)/(62) does not sufficiently distinguish the structures (61a) and (61b) to allow a definitive assignment of the product.

2.6 REACTION OF $[CODIr(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]$ WITH dppe

Treatment of $[CODIr(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]$ (51) with an equimolar quantity of dppe in $CDCl_3$ gives an immediate reaction with the *in situ* $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum indicating the initial formation of $[dppeIr(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]$ (63) [Equation 35].



(51)



(63)

----------[35]

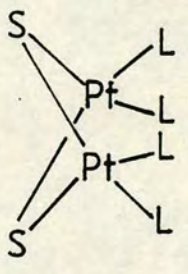
The spectrum shows two equally intense signals at δP_s 29.1 p.p.m. with $^1J_{PtP}$ 3510.7Hz and δP_p 34.8 p.p.m. The two sets of phosphorus atoms P_s,P_s, and P_p,P_p, are formally magnetically inequivalent but on the spectral width used to obtain the spectrum no $^2J_{pp}$ or $^3J_{pp}$ couplings were detected. Over a period of 30 minutes there is a disintegration of (63) which is accompanied by a colour change in the reaction solution from yellow → green → orange /brown. The principle decomposition species is identified as $[Ir(dppe)_2]^+$ (δP 50 p.p.m.) and some reformation of (51) is also observed.

2.7 REACTION OF $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ WITH $[CODMCl]_2$ (M=Rh,Ir)

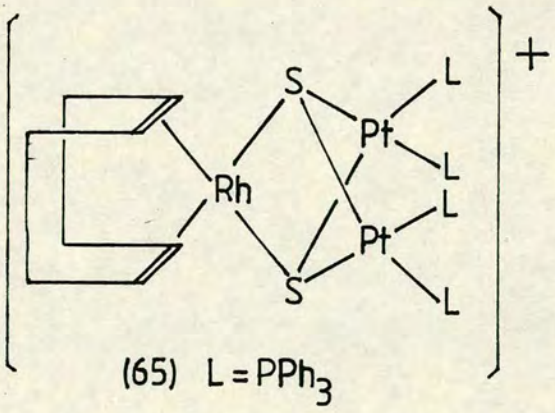
The reaction of cis-$[PtCl_2L_2]$ ($L=PPh_3, PPhMe_2$) with sodium sulphide generates the complex $[Pt_2(\mu\text{-}S)_2L_4]$ (64)[133].

X-ray studies show that (64) ($L=PPh_3, PPhMe_2$) are wedge-shaped molecules. The Pt centres are hinged together by sulphido bridges with an angle of 125° resulting between the two square planes. The lone electron pairs on the sulphido bridges are of sufficient basicity to form dative bonds to various metal ions forming metal-aggregates.[39,40,180] Reaction of (64) ($L=PPh_3$) with 0.5 equivalents of $[CODRhCl]_2$ in tetrahydrofuran followed by addition of methanolic NH_4PF_6 gives the triangular-heterobimetallic salt $[Pt_2Rh(\mu_3\text{-}S)_2(PPh_3)_4(COD)]PF_6$ (65)[123].

In the versatile reaction of $Ph_2P(S)H$ and $Pt(S_2CNEt_2)_2$ (Scheme 1) one of the products obtained is the diplatinum complex $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (8).



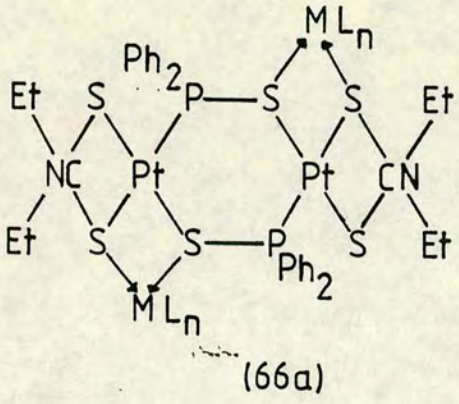
(64)



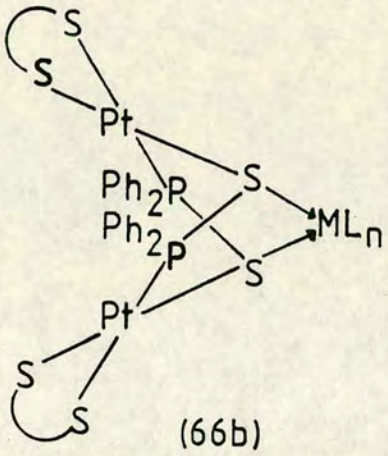
(65) $L=PPh_3$

It seemed likely that (8), like (64), could coordinate metal fragments utilising suitably-disposed sulphur atoms. Two modes of reaction not involving bridge destruction, could be envisaged for (8). In the solid state, the six-

membered ring $\overline{PtPSPtPS}$ adopts a chair conformation[26]. This conformation if retained during reaction may allow coordination of a metal ion(s) through the mutually-cis sulphur atoms of the dithiocarbamate ligand and the thiophosphorus bridge (66a). Alternatively if the ring adopts a skew-boat conformation, which produces an 'off-set' wedge arrangement in (8), coordination of a metal fragment by the bridging sulphur atoms appears a possibility (66b).



(66a)

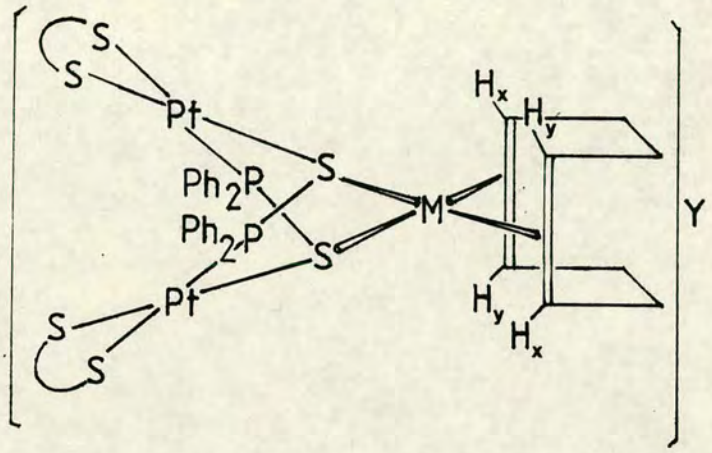


(66b)

The reaction of $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (8) with $[CODRhCl]_2$ in a respective 2:1 molar ratio proceeds rapidly at room temperature in $CDCl_3$ to give quantitative production of a single product. A yellow solid can be recovered following addition of either $NaBPh_4$ or NH_4PF_6 in methanol to the reaction solution. An analogous reaction occurs for (8) and $[CODIrCl]_2$ which yields on addition of methanolic $NaBPh_4$ an orange iridium complex. On the basis of multinuclear n.m.r., i.r., FAB mass spectral and micro-analytical data the yellow and orange products are formulated

as the trimetallic salts $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2MCOD\}Y$ ((67) M=Rh, $Y=PF_6^-$, BPh_4^-; (68) M=Ir, $Y=BPh_4^-$).

The $^{31}P-\{^1H\}$ n.m.r. spectra for (67) and (68) consist of superimposed signals from three separate isotopomers of

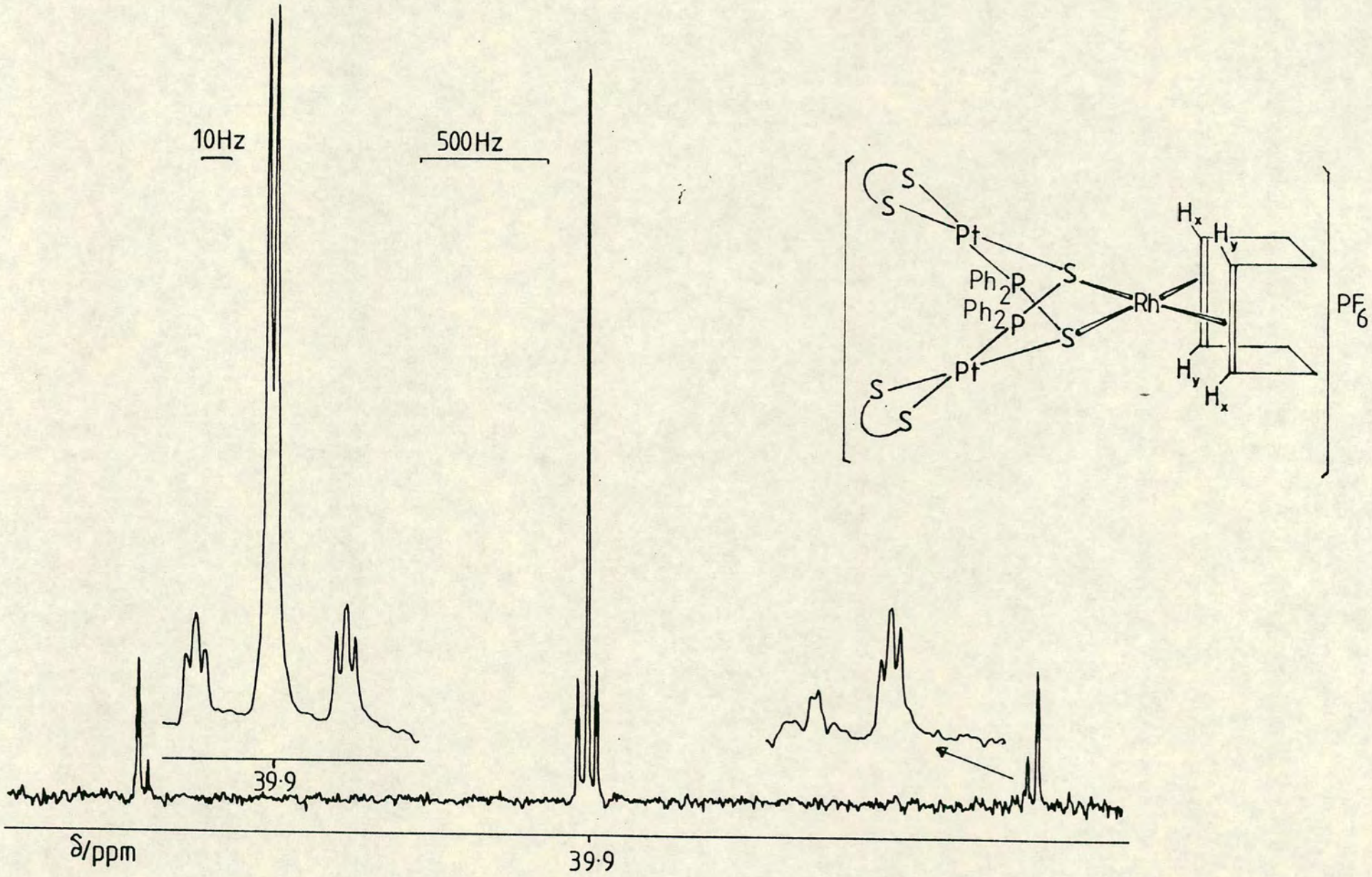


	M	Y
(67a)	Rh	PF_6^-
(67b)	Rh	BPh_4^-
(68)	Ir	BPh_4^-

S S = $S_2CNEt_2^-$

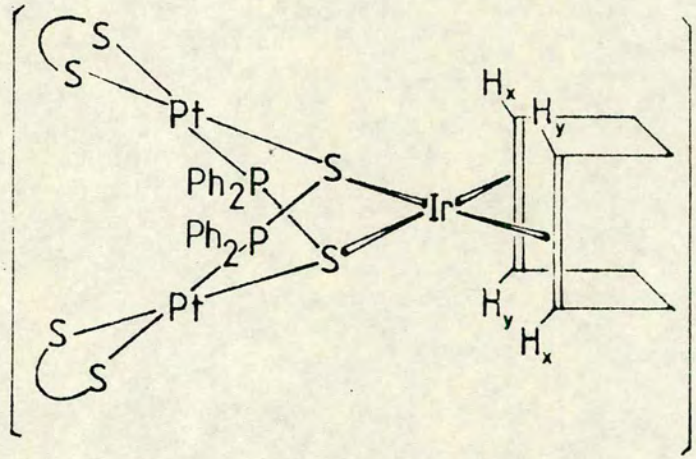
the diplatinum-trimetallic product (^{195}Pt only 33.3% abundant, $I=\frac{1}{2}$) with δP 39.9 p.p.m. for (67) and δP 46.3 p.p.m. for (68). In addition for (67a) (Figure 13, cation only) the signal for the isotopomer containing no ^{195}Pt nuclei (doublet at δP, ~4/9 spectral intensity); the isotopomer with a single ^{195}Pt nucleus (two doublets of overlapping doublets of doublets centred on δP, ~4/9 spectral intensity) and finally the isotopomer with two ^{195}Pt nuclei (second order AA'XX'M symmetrical about δP) all reveal a 4.1Hz doublet splitting. This splitting does not appear in the spectrum of the starting complex (8) and is of the correct magnitude for $^2J_{RhP}$ coupling. The characteristic ν_{PS} stretch, normally found for $L_nM(Ph_2PS)_2ML_n$ complexes in the region 600-575 cm^{-1} and identified at 578 cm^{-1} for (8), is not observed in the i.r. spectra

Figure 13: The $^{31}P-\{^{1}H\}$ n.m.r. specrum of $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2RhCOD\}PF_6$ (67a) in $CDCl_3$ at 298°K



of (67) and (68). A new band appears at low energy for (67) (550 cm^{-1}) and (68) (548 cm^{-1}), not identified for (8), which is likely to involve a ν_{PS} contribution and suggests a major complication involving the phosphine-sulphide bridges - such as metal coordination at sulphur. FAB mass spectra identify the parent cations (67a) (m/e 1332) and (68) (m/e 1422). Interestingly the spectra also reveal a common fragmentation path with loss of $[MCOD]^+$ ($RhCOD^+$, m/e 209; $IrCOD^+$, m/e 300) to the diplatinum species $[Pt(S_2CNEt_2)(Ph_2PS)]_2^+$ (m/e 1122). The ^1H n.m.r. spectra for the products (Figure 14 for (68)) show resonances for coordinated 1,5-COD and the diplatinum unit in the ratio 1:1 consistent with the formulations (67) and (68). The off-set wedge arrangement adopted by the diplatinum unit produces considerable assymetry in the 1,5-COD ligand. For both products two, equal-integral signals appear for the olefinic protons of the 1,5-COD ligand ((68) $\delta_{C\underline{H}}$ 4.44, 3.68 p.p.m.; (67) 4.63, 3.88 p.p.m.). A molecular model of (67-68) reveals that in an olefinic group one proton points toward a phenyl ring of the bridging phosphorus while the other points in the direction of the CN bond of the dithiocarbamate group. The two olefinic proton environments are depicted as H_x and H_y in (67-68). A similar situation exists for the methylene protons of the 1,5-COD ligand with three signals observed for (68) ($\delta C\underline{H}_2$ 1.90(4H), 1.58(2H) and 1.28(2H) p.p.m.) and two for (67) ($\delta C\underline{H}_2$ 2.00(4H) and 1.47(4H) p.p.m.). The methyl groups for the diethyl-dithiocarbamate ligands appear as overlapping triplets giving

Figure 14: The ^1H n.m.r. spectrum of {[Pt(S_2CNEt_2)(Ph_2PS)]$_2$IrCOD}BPh_4 (68) in $CDCl_3$ at 298°K



a quintet for (68) (δCH_3 1.09, 1.16 p.p.m.) and a quartet for (67) (δCH_3 1.21, 1.26 p.p.m.). Interestingly the methylene resonances appear more complicated than would be expected for overlapping quartets. The complicity may result from overlapping ABM_3 patterns brought about through hindered rotation in the CN bond of the dithiocarbamate ligand. An increase in the ν_{CN} stretching frequency in the i.r. spectra for (67) and (68) of about 15 cm^{-1} compared to ν_{CN} for (8) supports an increase in the double bond character of the CN bond.

The equimolar reaction of (8) and $[CODMCl]_2$ (M=Rh,Ir) gives the trimetallic products (67) and (68) and unreacted $[CODMCl]_2$.

Treatment of (67) with CO in $CDCl_3$ under ambient conditions gave no reaction. This is in contrast to the facile displacement of the 1,5-COD ligand by CO in the complexes (48), (52) and (54) but is in line with observations of other workers who found no tendency for 1,5-COD substitution when the rhodium centre has an additional large bulky ligand [123,134].

2.8 CONCLUSIONS

A range of phosphine chalcogenide dibridged heterobimetallic complexes containing the cyclooctadiene ligand have been prepared. In most cases the organic ligand can be replaced to give derivatives containing carbonyl and phosphine ligands. The ability of these heterobimetallic complexes to engage in oxidative addition reactions at either or both metal centres was not investigated.

2.9.1 EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the 4000-250 cm^{-1} region on a Perkin-Elmer 557 grating spectrometer either as Nujol mulls on caesium iodide plates or as potassium bromide discs. Hydrogen-1 and carbon-13 n.m.r. (proton noise decoupled) spectra were recorded on a Bruker WP200SY spectrometer and phosphorus-31 n.m.r. spectra (proton noise decoupled) on a Jeol FX-60Q spectrometer operating in the pulse and Fourier transform mode at 24.24MHz with chemical shifts reported in p.p.m. to high frequency of 85% H_3PO_4. Mass spectra were recorded on a Kratos MS-50TC spectrometer using Fast Atom Bombardment ionisation from a DMF/thioglycerol matrix. Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298K. Melting points were determined with a Kofler hot-stage microscope and are uncorrected, and molecular weights were determined on a Perkin-Elmer Hitachi Model 115 osmometer calibrated with benzil.

2.9.2 MATERIALS

Potassium tetrachloroplatinate(II), rhodium(III) chloride trihydrate, iridium(III) chloride trihydrate (Johnson Matthey PLC), cycloocta-1,5-diene (BDH Chemicals), sodium diethyldithiocarbamate, diphenylphosphinous chloride and anhydrous sodium methoxide (Aldrich) were used as supplied.

Other materials were prepared by standard literature methods: $NaS_2CN^iPr_2.2H_2O$ [128], Ph_2PH [135], $Ph_2P(S)H$ [136], $[Pt(S_2CNR_2)_2]$ (R=Et,^{i}Pr) [137], $[CODMCl]_2$ M=Rh [98], Ir [99]), $[CODRh(PPh_3)_2]BPh_4$ [138] and all other platinum complexes[5,26].

Initial reactions were normally performed in situ on a n.m.r. scale and if successful carried out on a larger scale under dry nitrogen using degassed solvent.

Crystal data for $[CODRh(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]$ (48)

$C_{37}H_{42}NS_4P_2RhPt$, M=988.93 Orthorhombic.
a = 22.533(13), b = 22.817(17), C = 14.690(15)Å, $\alpha = \beta = \gamma = 90°$ U = 7552.6Å^3, Z = 8, D_c = 1.739 gcm^{-3}, Space group P_{ccn}, Mo-K_α radiation, λ = 0.71069Å, Mu = 108.48 cm^{-1}, F(000) = 3904, T = 293°K. The structure solution and refinement were based on 2679 observed ($I>6\sigma(I)$) reflections (6554 measured) from a Stoe-Stadi 2 diffractometer to give final R and R_w values of 0.0486 and 0.0366 respectively.

Crystal data for $[CODIr(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]$ (51)

$C_{39}H_{46}NS_4P_2IrPt$, M=1106.3 Monoclinic
a = 11.873(4), b = 23.064(9), C = 15.609, β = 107.826(25)
U = 4069Å^3, Z = 4, D_c 1.806gcm^{-3}, Space group $P_{2_{i/c}}$ Mo-K_α radiation, λ = 0.71069Å, Mu = 69.94 cm^{-1}, F(000) = 2144, T = 295°K. The structure solution and refinement were based on 4612 observed ($I>6\sigma(I)$) reflections (7132 measured) from a Stoe-Stadi 2 diffractometer to give R and R_w values of 0.0534 and 0.0712 respectively.

2.9.5 COMPLEXES

Preparation of heterobimetallics [CODM(I)(μ-$SPPh_2$)$_2$Pt(II)-(S_2CNR_2)] (48-51) [CODRh(μ-$SPPh_2$)$_2$Pt(S_2CNEt_2)] (48). $[NH_2Et_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (86 mg, 0.1 mmol) and $[CODRhCl]_2$ (26 mg, 0.05 mmol) were stirred in chloroform (8 ml) for five minutes at room temperature. Addition of methanol (25 ml) precipitated a pale yellow solid which was collected by filtration, washed with cold methanol (10 ml) and diethylether (10 ml) and finally dried *in vacuo* at 60°C for several hours. Yield 83 mg, 84%. Melting point 208°C (decomposition). Found: C, 45.17; H, 4.24; N, 1.41; m/e 990 $(M+1)^+$ FAB mass spec. Calculated for $C_{37}H_{42}NS_4P_2RhPt$ C, 44.94; H, 4.28; N, 1.42; 989.9 MWt. KBr disc i.r. spectrum ν_{CN} 1512, ν_{PS} 595 cm^{-1}.

[CODRh(μ-$SPPh_2$)$_2$Pt($S_2CN^iPr_2$)] (49). Prepared as above using $[NH_2{}^iPr_2][Pt(S_2CN^iPr_2)(Ph_2PS)_2]$ (184 mg, 0.2 mmol) and $[CODRhCl]_2$ (50 mg, 0.1 mmol). Yield 140 mg, 69%. Melting point 212°C (decomposition). Found, C, 45.83; H, 4.53; N, 1.49; Calc. for $C_{39}H_{46}NS_4P_2RhPt$, C, 46.06; H, 4.56; N, 1.38. KBr disc i.r. spectrum ν_{CN} 1494, ν_{PS} 591 cm^{-1}.

[CODIr(μ-$SPPh_2$)$_2$Pt(S_2CNEt_2)] (50). Prepared as above using $[NH_2Et_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (83 mg, 0.098 mmol) and $[CODIrCl]_2$ (33 mg, 0.049 mmol). Yield 85 mg, 80%. Melting point 215°C (decomposition). Found: C, 40.69; H, 3.88; N, 1.30; Calc. for $C_{37}H_{42}NS_4P_2IrPt$, C, 41.22; H, 3.93; N, 1.30. kBr disc i.r. spectrum ν_{CN} 1510, ν_{PS} 587 cm^{-1}.

[CODIr(μ-$SPPh_2$)$_2$Pt($S_2CN^iPr_2$)] (51). Prepared as above

using $[NH_2{}^iPr_2][Pt(S_2CN{}^iPr_2)(Ph_2PS)_2]$ (83 mg, 0.092 mmol) and $[CODIrCl]_2$ (31 mg, 0.046 mmol). Yield 81 mg, 80%. Melting point 222°C (decomposition). Found, C, 41.64; H, 3.97; N, 1.19; Calc. for $C_{39}H_{46}NS_4P_2IrPt$, C, 42.34; H, 4.19; N, 1.26. KBr disc i.r. spectrum, ν_{CN} 1496, ν_{PS} 590 cm^{-1}.

Preparation of the heterobimetallics $[CODM(I)(\mu\text{-}OPPh_2)(\mu\text{-}SPPh_2)Pt(II)(S_2CNR_2)]$ (52-53) $[CODRh(\mu\text{-}OPPh_2)(\mu\text{-}SPPh_2)Pt(S_2CNEt_2)]$ (52). $[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)H]$ (78 mg, 0.1 mmol) dissolved in chloroform (8 ml) was treated with six drops of triethylamine (excess). $[CODRhCl]_2$ (26 mg, 0.05 mmol) was then added and the reaction solution stirred for five minutes at room temperature. Methanol (25 ml) was added and the solution stirred at 0°C for a further ten minutes to precipitate the bright-yellow product which was collected, washed with cold methanol (10 ml) and pet.ether 40-60° (5 ml), and dried *in vacuo* at 60°C for several hours. Yield 75 mg, 77%. Melting point 183°C. Found, C, 45.00; H, 4.25; N, 1.61. Calc. for $C_{37}H_{42}NS_3OP_2RhPt$, C, 45.68; H, 4.35; N, 1.44. KBr disc i.r. spectrum ν_{CN} 1505, ν_{PO} 1020, ν_{PS} 582 cm^{-1}. $[CODIr(\mu\text{-}OPPh_2)(\mu\text{-}SPPh_2)Pt(S_2CNEt_2)]$ (53). Prepared as above using $[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)H]$ (100 mg, 0.13 mmol) and $[CODIrCl]_2$ (44 mg, 0.065 mmol). Yield 90 mg, 65%. Melting point 195°C (decomposition). Found, C, 41.00; H, 4.10; N, 1.69. Calc. for $C_{37}H_{42}NS_3OP_2RhPt$, C, 41.85; H, 3.99; N, 1.32.

Preparation of heterobimetallics [CODM(I)(μ-$OPPh_2$)$_2$-$Pt(S_2CNEt_2)$] (54-55). [CODRh(μ-$OPPh_2$)$_2$$Pt(S_2CNEt_2)$] (54). $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ (353 mg, 0.47 mmol) dissolved in methylene chloride (15 ml) was treated with anhydrous sodium methoxide (54 mg, 1 mmol) to form the 'oxyring' anion $[Pt(S_2CNEt_2)(Ph_2PO)_2]^-$ *in situ*. $[CODRhCl]_2$ (120 mg, 0.24 mmol) was then added and the reaction solution stirred for 10-15 minutes. The solution was filtered through a celite pad to remove the NaCl which had formed and methanol (40 ml) added to the filtrate. The resultant solution was stirred at 0°C for a further 15 minutes to precipitate the light-yellow product which was collected, washed with cold methanol (10 ml), and dried *in vacuo* at 60°C for 4 hours. Yield 410 mg, 91%. Found, C, 46.36; H, 4.45; N, 1.59; Calc. for $C_{37}H_{42}NS_2O_2P_2RhPt$, C, 46.44; H, 4.42; N, 1.46. KBr disc i.r. spectrum ν_{CN} 1505, ν_{PO} 1050 cm^{-1} [CODIr(μ-$OPPh_2$)$_2$-$Pt(S_2CNEt_2)$] (55). Prepared as above using $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$/NaOMe and $[CODIrCl]_2$. Some decomposition occured during the preparation which denied the recovery of an analytically pure material.

Preparation of heterobimetallics $[(OC)_2M(I)(\mu\text{-}XPPh_2)$-($\mu$-$YPPh_2$)$Pt(II)(S_2CNEt_2)]$ (56-59) $[(OC)_2Rh(\mu\text{-}SPPh_2)_2$-$Pt(S_2CNEt_2)]$ (56). A chloroform solution (8 ml) containing $[CODRh(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]$ (40 mg) was treated with carbon monoxide for 100 seconds during which time a strong smell of diene developed [Note CO inhalation fatal]. Addition of diethylether (25 ml) to the reaction solution, followed by

trituration precipitated a pale yellow solid, which was collected washed with diethylether (5 ml) and dried *in vacuo* at 60°C for 3 hours. Yield 30 mg, 79%. Melting point 176°C (decomposition). Found, C, 38.06; H, 3.17; N, 1.64; Calc. for $C_{31}H_{30}NS_4O_2P_2RtPt$, C, 39.75; H, 3.23; N, 1.50. KBr disc i.r. spectrum ν_{CN} 1520, ν_{PS} 583, ν_{CO} 2053, 1993 cm^{-1}; CH_2Cl_2 solution ν_{CO} 2062, 1998 cm^{-1}.

[(OC)$_2$Rh(μ-OPPh$_2$)(μ-SPPh$_2$)Pt(S$_2$CNEt$_2$)] (57). Prepared as above using [CODRh(μ-OPPh$_2$)(μ-SPPh$_2$)Pt(S$_2$CNEt$_2$)] and CO. Yield 86%. Melting point 175°C (decomposition). Found, C, 40.10; H, 3.39; N, 1.72; Calc for $C_{31}H_{30}NS_3O_3P_2RhPt$, C, 40.43; H, 3.28; N, 1.52. KBr disc i.r. spectrum ν_{CN} 1515, ν_{PS} 575, ν_{PO} 1010, ν_{CO} 2065, 1995 cm^{-1}.

[(OC)$_2$Rh(μ-OPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (58). Prepared as above using [CODRh(μ-OPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] and CO. Yield 52%. Not obtained analytically pure. Found, C, 38.9; H, 3.42; N, 2.3; Calc. for $C_{31}H_{30}NS_2O_4P_2RhPt$, C, 41.2; H, 3.3; N, 1.6. KBr disc i.r. spectrum ν_{CN} 1505, ν_{PO} 1052, ν_{CO} 2078, 1997 cm^{-1}, CH_2Cl_2 solution ν_{CO} 2075, 2000 cm^{-1}.

[(CO)$_2$Ir(μ-OPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (59). Prepared as above using [CODIr(μ-OPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] and CO. Observed *in situ* only. CH_2Cl_2 solution i.r. spectrum ν_{CO} 2060, 1984 cm^{-1}.

Preparation of heterobimetallics [(OC)(Ph$_3$P)Rh(I)(μ-XPPh$_2$)-(μ-YPPh$_2$)Pt(II)(S$_2$CNEt$_2$)] (60-62)

[(OC)(Ph$_3$P)Rh(μ-SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (60). Prepared by the equimolar reaction of [(OC)$_2$Rh(μ-SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] and PPh_3 in chloroform. However a more convenient 'one-pot' synthesis involved treatment of [CODRh(μ-SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (100 mg, 0.1 mmol) with CO in $CDCl_3$ (2 ml) to form

$[(CO)_2Rh(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]$ (94 mg based on quantitative conversion) *in situ* with addition of triphenylphosphine (26 mg, 0.1 mmol) resulting in the vigorous evolution of gas. n-Pentane (10 ml) was then added to the golden-yellow reaction solution to precipitate the light-brown product, which was collected, washed with n-pentane (5 ml) and dried *in vacuo* at 60°C for 2 hours. Yield 81 mg, 71%. Found, C, 49.00; H, 3.82; N, 1.31; m/e 1143 $[(M\text{-}CO)+1]^+$ FAB mass spec; calc. for $C_{48}H_{45}NS_4OP_3RhPt$, C, 49.20; H, 3.87; N, 1.20; 1170 mwt. KBr disc i.r. spectrum ν_{CN} 1512, ν_{PS} 592, ν_{CO} 1972 cm^{-1}. $^{31}P\text{-}\{^1H\}$ n.m.r. data at R.T. in $CDCl_3$. First order ABX spectrum with additional metal nuclei coupling. δP (thiophosphorus bridges) 33.9, 25.9 p.p.m., $^1J_{PtP}$ 3510.0, $^2J_{PP}$ 23.6, $^3J_{PPPh_3}$ 8.4, 17.5, $^2J_{RhP}$ (on low-frequency side of AB only) 3.0Hz; δP_{PPh_3} 39.6 p.p.m., $^1J_{RhP}$ 159.4Hz, ^1H n.m.r. data (R.T./$CDCl_3$). Dithiocarbamate ligand: overlapping quartets (δ_{CH_2} 3.47, 3.54 p.p.m.) and triplets (1.19, 1.20 p.p.m.). Phenyl region 7.06-7.90 p.p.m.: broad multiplets due to phosphorus substituents. *[(OC)(Ph$_3$P)Rh(μ-OPPh$_2$)(μ-SPPh$_2$)Pt(S$_2$CNEt$_2$)] (61)*. Prepared as above using $[CODRh(\mu\text{-}OPPh_2)(\mu\text{-}SPPh_2)Pt\text{-}(S_2CNEt_2)]$/CO and PPh_3. Yield 75%. Found, C, 49.28; H, 3.97; N, 1.31; Calc. for $C_{48}H_{45}SN_3O_2P_3RhPt$, C, 49.88; H, 3.92; N, 1.22. KBr disc i.r. spectrum ν_{CN} 1512, ν_{PS} 580, ν_{PO} 1042, ν_{CO} 1958 cm^{-1}. $^{31}P\text{-}\{^1H\}$ n.m.r. data (R.T./$CDCl_3$). δP_s 25.6 p.p.m., $^1J_{PtPs}$ 3537.6, $^2J_{RhPs}$ 3.7, $^2J_{PsPo}$ 31.7, $^3J_{PPh_3Ps}$ 6.1Hz; δPo 58.0 p.p.m., $^1J_{PtPo}$ 3651.7, $^2J_{RhPo}$ 3.7Hz; δP_{PPh_3} 35.6, $^1J_{PhP}$ 166.0Hz.

[(OC)(Ph$_3$P)Rh(μ-OPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (62). Prepared as

above using $[CODRh(\mu\text{-}OPPh_2)_2Pt(S_2CNEt_2)]$/CO and PPh_3. Not obtained analytically or spectrochemically pure. KBr disc i.r. spectrum ν_{CN} 1511, ν_{PO} 1042, ν_{CO} 1971 cm^{-1}. $^{31}P\text{-}\{^1H\}$ n.m.r. data (R.T./$CDCl_3$) spectrum shows an AB pattern centred at δP 58.8 p.p.m., $^1J_{PtP}$ 3730.7, $^2J_{PP}$ 30.6, $^2J_{RhP}$ (on low frequency side of AB only) 2.0Hz; δP_{PPh_3} 48.7, $^1J_{RhP}$ 183.1Hz.

Preparation of $[(dppe\text{-}P,P)Ir(I)(\mu\text{-}SPPh_2)_2Pt(II)(S_2CN^iPr_2)]$ (63). Observed in situ only during initial reaction of equimolar quantities of $[CODIr(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]$ (29 mg, 0.025 mmol) and diphenylphosphinoethane (11 mg, 0.027 mmol) in $CDCl_3$ at room temperature. $^{31}P\text{-}\{^1H\}$ n.m.r. data (R.T./$CDCl_3$) δP_s 29.1 p.p.m., $^1J_{PtPs}$ 3510.7Hz; δP_P 34.8 p.p.m.

Preparation of the trimetallic salts $\{[Pt(II)(S_2CNEt_2)\text{-}(Ph_2PS)]_2Rh(I)COD\}Y$ (67-68)

$\{[Pt(S_2CNEt_2)(Ph_2PS)]_2RhCOD\}PF_6$ (67a). $[Pt(S_2CNEt)(Ph_2PS)]_2$ (110 mg, 0.098 mmol) and $[CODRhCl]_2$ (24 mg, 0.049 mmol) were stirred at room temperature in chloroform (8 ml) for 5 minutes. A methanolic solution (15 ml) of NH_4PF_6 (20 mg, 0.18 mmol) was then added to precipitate the yellow product which was collected, washed with cold methanol (3x5 ml) and dried in vacuo at 60°C for 4 hours. Yield 104 mg, 72%. Melting point 230°C. Found, C, 33.6; H, 3.39; N, 2.11; m/e 1332 $(M+1)^+$ FAB mass spec; Calculated for $C_{42}H_{52}N_2S_6P_3F_6RhPt_2$, C, 34.2; H, 3.55; N, 1.90; 1331 mwt cation. KBr disc i.r. spectrum ν_{CN} 1526, ν_{PF_6} 838, 'ν_{PS}' 550 cm^{-1}. The yellow BPh_4^- salt could also be isolated by addition of methanolic $NaBPh_4$ to the reaction

solution {[Pt(S_2CNEt_2)(Ph_2PS)]$_2$RhCOD}BPh_4 (67b). Yield 81%; Found, C, 48.8; H, 4.31; N, 1.73; Calc. for $C_{66}H_{72}N_2S_6P_2BRhPt_2$, C, 48.0; H, 4.39; N, 1.70. KBr disc i.r. spectrum ν_{CN} 1528, 'ν_{PS}' 549 cm^{-1}.

{[Pt(S_2CNEt_2)(Ph_2PS)]$_2$IrCOD}BPh_4 (68). Prepared as above using [Pt(S_2CNEt_2)(Ph_2PS)]$_2$ (41 mg, 0.037 mmol) and [CODIrCl]$_2$ (12 mg, 0.018 mmol) followed by addition of methanolic $NaBPh_4$ to yield the orange product. Yield 50 mg, 78%. Melting point >230°C. Found, C, 44.6; H, 4.05; N, 1.50; m/e 1422 $(M+1)^+$ FAB mass spec; Calc. for $C_{66}H_{72}N_2S_6P_2BIrPt_2$, C, 45.5; H, 4.17, N, 1.61; 1422 mwt cation. KBr disc i.r. spectrum ν_{CN} 1530, 'ν_{PS}' 548 cm^{-1}.

TABLE 2. PHOSPHORUS-31-{^{1}H} N.M.R. DATA[j] FOR HETEROMETALLIC COMPLEXES PREPARED IN CHAPTER 2 SPECTRA OBTAINED IN $CDCl_3$ AT 298°K

COMPLEX	δP	$^1J_{PtP}$	$^2J_{RhP}$	$^2J_{PP}$
(48) $[CODRh(SPPh_2)_2Pt(S_2CNEt_2)]$[a]	31.9[f]	3488.8	1.7	-
(49) $[CODRh(SPPh_2)_2Pt(S_2CN^iPr_2)]$[a]	32.6[f]	3432.6	1.7	-
(50) $[CODIr(SPPh_2)_2Pt(S_2CNEt_2)]$[b]	29.2[f]	3449.7	-	-
(51) $[CODIr(SPPh_2)_2Pt(S_2CN^iPr_2)]$[b]	29.7[f]	3401.1	-	-
(52) $[CODRh(SPPh_2)(OPPh_2)Pt(S_2CNEt_2)]$[c]	24.0[f]	3496.1	3.0	30.3
	62.2[g]	3647.5	3.9	
(53) $[CODIr(SPPh_2)(OPPh_2)Pt(S_2CNEt_2)]$[d]	15.6[f]	3420.4	-	31.7
	66.0[g]	3652.3		
(54) $[CODRh(OPPh_2)_2Pt(S_2CNEt_2)]$[a]	59.2[g]	3710.9	1.8	-
(55) $[CODIr(OPPh_2)_2Pt(S_2CNEt_2)]$[b]	60.8[g]	3671.8	-	-
(56) $[(OC)_2Rh(SPPh_2)_2Pt(S_2CNEt_2)]$[a]	30.7[f]	3488.3	2.4	-
(57) $[(OC)_2Rh(SPPh_2)(OPPh_2)Pt(S_2CNEt_2)]$[c]	21.4[f]	3492.9	4.4	30.9
	70.6[g]	3662.1	4.4	
(58) $[(OC)_2Rh(OPPh_2)_2Pt(S_2CNEt_2)]$[a]	65.4[g]	3691.4	1.8	-
(59) $[(OC)_2Ir(OPPh_2)_2Pt(S_2CNEt_2)]$[b]	66.9[g]	3659.7	-	-
(67a) $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2RhCOD\}PF_6$[e,h]	39.9[f]	3622.2	4.1	5.2
(68) $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2IrCOD\}BPh_4$[e,i]	46.3[f]	3598.6	-	6.2

Notes: a Spectrum a 1.4.1 t of d. b Spectrum a 1.4.1 t. c Spectrum comprises two sets of 1.4.1 t of d of d. d Spectrum comprises two sets of 1.4.1 t of d. e Superimposed signals from 3 isotopomers. f δP_s (thiophosphorus resonance). g δP_o (oxyphosphorus resonance). h $^2J_{PtP}$ 75.1Hz. i $^2J_{PtP}$ 74.5Hz. j δP/ppm; J/Hz.

TABLE 3. HYDROGEN-1 N.M.R. DATA FOR HETEROBIMETALLIC COMPLEXES PREPARED IN CHAPTER 2 SPECTRA OBTAINED IN $CDCl_3$ AT 298°K AT 298°K. δH/ppm

COMPLEX	1,5-COD			$^{a}S_2CNR_2^-$		
	δCH	δCH_2		$\delta CH_2/CH$	δCH_3	δPh
(48) $[CODRh(SPPh_2)_2Pt(S_2CNEt_2)]$	3.98m	2.15m	1.71m[b]	3.54q	1.12t	7.25-7.86m
(49) $[CODRh(SPPh_2)_2Pt(S_2CN^iPr_2)]$	3.98m	2.20m	1.69m[b]	4.30br	1.28d	7.26-7.86m
(50) $[CODIr(SPPh_2)_2Pt(S_2CNEt_2)]$	3.54m	2.00m	1.44m[b]	3.44q	1.12t	7.25-7.82m
(51) $[CODIr(SPPh_2)_2Pt(S_2CN^iPr_2)]$	3.54m	2.00m	1.44m[b]	4.30br	1.28d	7.25-7.82m
(52) $[CODRh(SPPh_2)(OPPh_2)Pt(S_2CNEt_2)]$	3.80m	2.30m	1.70m[c]	3.50q	1.12t	7.11-7.83m
	3.64m	2.15m	1.55m	3.47q	1.15t	
(54) $[CODRh(OPPh_2)_2Pt(S_2CNEt_2)]$	3.66m	2.36m	1.55m[b]	3.51q	1.15t	7.19-7.67m
(56) $[(OC)_2Rh(SPPh_2)_2Pt(S_2CNEt_2)]$	-	-	-	3.49q	1.16t	7.25-7.85m
(67a) $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2RhCOD\}PF_6$	4.63m	2.00m	1.47m[d]	3.52m	1.21t	7.20-8.4m
	3.88m				1.26t	
(68) $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2IrCOD\}BPh_4$	4.44m	1.90m	1.52m[d]	3.32m	1.16t	6.8 -8.2m
	3.68m		1.28m		1.09t	

Notes: a Triplet and quartet splittings invariably $^3J_{HH}$ 7.2Hz, doublet splitting invariably $^3J_{HH}$ 6.6Hz. b See Figure 2. c See Figure 12. d See (67a) and (68) in text.

TABLE 4: CARBON-13-{^{1}H} N.M.R. DATA FOR THE HETEROMETALLIC COMPLEXES PREPARED IN CHAPTER 2. SPECTRA OBTAINED IN $CDCl_3$ AT 298°K δ_C/ppm; J/Hz

COMPLEX	δCH	$^1J_{RhC}$	δCH_2	$\delta CH_2/\delta CH$	δCH_3	δCN	δPh
(48) $[CODRh(SPPh_2)_2Pt(S_2CNEt_2)]$	81.93	11.6	30.94	43.86	12.20	205.82	127.2-138.7
(49) $[CODRh(SPPh_2)_2Pt(S_2CN^iPr_2)]$	81.84	11.6	30.91	50.91	19.64	204.93	127.1-138.7
(50) $[CODIr(SPPh_2)_2Pt(S_2CNEt_2)]$	66.28	-	31.51	43.89	12.18	205.46	126.6-137.8
(51) $[CODIr(SPPh_2)_2Pt(S_2CN^iPr_2)]$	66.25	-	31.51	51.02	19.65	204.70	127.2-137.9
(52) $[CODRh(SPPh_2)(OPPh_2)Pt(S_2CNEt_2)]$	84.85[a]	11.6	31.88	44.26	12.22	206.70	127.0-140.6
	70.65[b]	14.1	29.50	43.63			
(54) $[CODRh(OPPh_2)_2Pt(S_2CNEt_2)]$	74.87	14.0	30.57	43.96	12.24	207.24	127.1-141.4
(67a) $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2RhCOD\}PF_6$[c]	86.7	11.1	32.89	44.92	12.28	202.72[d]	128.3-134.3
	85.8	10.8	28.20	44.50	12.21		

Notes: a Olefinic group trans to s. b Olefinic group trans to o. c Contaminated by some unreacted $[CODRhCl]_2$ δ_{CH} 75.5p.p.m., $^1J_{RhH}$ 13.8Hz δ_{CH_2} 30.7 p.p.m. d $^2J_{PtC}$ observed 107.8Hz.

Table 5: Bond distances (Å) with standard deviations in parenthesis for [CODRh(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (48)

Rh(1) - S(1)	2.328(4)	Pt(1) - S(3)	2.359(4)
Rh(1) - S(2)	2.370(4)	Pt(1) - S(4)	2.376(4)
Rh(1) - C(1)	2.173(14)	Pt(1) - P(1)	2.261(4)
Rh(1) - C(2)	2.112(15)	Pt(1) - P(2)	2.273(4)
Rh(1) - C(5)	2.179(16)	S(3) - C(1N)	1.730(14)
Rh(1) - C(6)	2.153(15)	S(4) - C(1N)	1.700(14)
S(1) - P(1)	2.049(5)	C(1N) - N(1)	1.327(18)
S(2) - P(2)	2.042(5)	N(1) - C(11)	1.452(19)
C(1) - C(2)	1.427(20)	N(1) - C(21)	1.475(21)
C(1) - C(8)	1.520(20)	C(11) - C(12)	1.504(23)
C(2) - C(3)	1.516(22)	C(21) - C(22)	1.51(3)
C(3) - C(4)	1.513(23)	P(1) - C(31)	1.820(10)
C(4) - C(5)	1.501(23)	P(1) - C(41)	1.805(10)
C(5) - C(6)	1.371(22)	P(2) - C(51)	1.836(8)
C(6) - C(7)	1.474(22)	P(2) - C(61)	1.847(9)
C(7) - C(8)	1.526(22)		

Table 6: Selected bond angles (°) with standard deviations in parenthesis for [CODRh(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (48)

S(1) - Rh(1) - S(2)	94.92(14)	S(1) - P(1) - Pt(1)	117.42(21)
Rh(1) - S(1) - P(1)	114.70(21)	S(2) - P(2) - Pt(1)	122.90(20)
Rh(1) - S(2) - P(2)	103.47(19)	S(1) -Rh(1) - C(5)	86.7(4)
S(3) - Pt(1) - S(4)	74.05(14)	S(1) -Rh(1) - C(6)	88.8(4)
S(3) - Pt(1) - P(1)	95.97(14)	S(2) -Rh(1) - C(1)	90.5(4)
S(4) - Pt(1) - P(2)	96.85(14)	S(2) -Rh(1) - C(2)	89.7(4)
P(1) - Pt(1) - P(2)	93.33(13)	C(1) -Rh(1) - C(2)	38.9(5)
Pt(1) - S(3) - C(1N)	86.6(5)	C(5) -Rh(1) - C(6)	36.9(6)
Pt(1) - S(4) - C(1N)	86.7(5)	C(1) -Rh(1) - C(6)	81.7(5)
S(3) - C(1N) - S(4)	112.5(8)	C(1) -Rh(1) - C(5)	91.4(6)
S(3) - C(1N) - N(1)	123.1(11)	C(2) -Rh(1) - C(6)	96.7(6)
S(4) - C(1N) - N(1)	124.4(11)	C(2) -Rh(1) - C(5)	82.4(6)

Table 7: Bond distances (Å) with standard deviations in parentheses for [CODIr(SPPh$_2$)$_2$Pt(S$_2$CN^{i}Pr$_2$)] (51)

Ir(1)	S(1)	2.315(4)	Pt(1)	S(3)	2.368(4)
Ir(1)	S(2)	2.379(4)	Pt(1)	S(4)	2.351(4)
Ir(1)	C(1)	2.162(16)	Pt(1)	P(1)	2.257(4)
Ir(1)	C(2)	2.129(17)	Pt(1)	P(2)	2.274(4)
Ir(1)	C(5)	2.181(20)	S(3)	C(1N)	1.734(15)
Ir(1)	C(6)	2.134(20)	S(4)	C(1N)	1.714(15)
S(1)	P(1)	2.056(5)	C(1N)	N(1)	1.321(20)
S(2)	P(2)	2.041(5)	N(1)	C(11)	1.47(3)
C(1)	C(2)	1.388(24)	N(1)	C(21)	1.50(3)
C(1)	C(8)	1.51(3)	C(11)	C(12)	1.43(4)
C(2)	C(3)	1.55(3)	C(11)	C(13)	1.54(3)
C(3)	C(4)	1.48(3)	C(21)	C(22)	1.44(4)
C(4)	C(5)	1.56(3)	C(21)	C(23)	1.43(4)
C(5)	C(6)	1.36(3)	P(1)	C(31)	1.826(10)
C(6)	C(7)	1.51(3)	P(1)	C(41)	1.806(11)
C(7)	C(8)	1.55(3)	P(2)	C(51)	1.817(11)
			P(2)	C(61)	1.813(11)

Table 8: Selected bond angles (°) with standard deviations in parentheses for [CODIr(SPPh$_2$)$_2$Pt(S$_2$CN^{i}Pr$_2$)] (51)

S(1)	Ir(1) S(2)	94.77(13)	S(1)	P(1) Pt(1)	114.74(19)
Ir(1)	S(1) P(1)	113.48(20)	S(2)	P(2) Pt(1)	120.97(19)
Ir(1)	S(2) P(2)	105.06(18)	S(1)	Ir(1) C(5)	86.0(5)
S(3)	Pt(1) S(4)	73.84(14)	S(1)	Ir(1) C(6)	87.7(6)
S(3)	Pt(1) P(1)	97.40(13)	S(2)	Ir(1) C(1)	91.7(4)
S(4)	Pt(1) P(2)	96.49(14)	S(2)	Ir(1) C(2)	88.3(5)
P(1)	Pt(1) P(2)	92.32(13)	C(1)	Ir(1) C(2)	37.7(6)
Pt(1)	S(3) C(1N)	87.1(5)	C(5)	Ir(1) C(6)	36.8(8)
Pt(1)	S(4) C(1N)	88.2(5)	C(1)	Ir(1) C(6)	81.9(7)
S(3)	C(1N) S(4)	110.6(8)	C(1)	Ir(1) C(5)	92.4(7)
S(3)	C(1N) N(1)	124.0(11)	C(2)	Ir(1) C(6)	96.7(7)
S(4)	C(1N) N(1)	125.5(10)	C(2)	Ir(1) C(5)	83.9(7)

CHAPTER 3

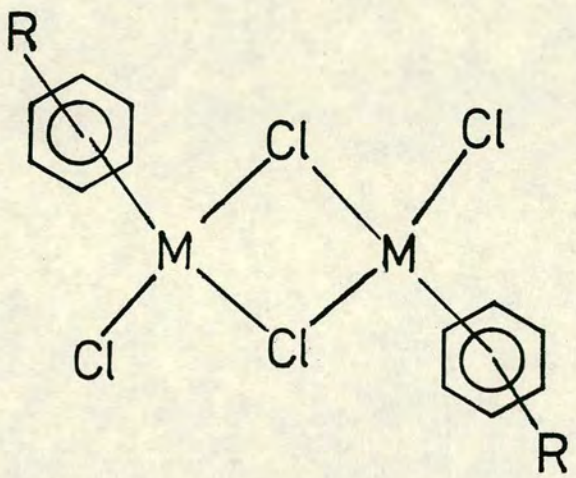
REACTION OF PLATINUM COMPLEXES CONTAINING SECONDARY PHOSPHINE CHALCOGENIDE LIGANDS WITH $[(arene)MCl_2]_2$ (M=Ru(II),Os(II)) AND $[(C_5Me_5)MCl_2]_2$ (M=Rh(III),Ir(III))

3.1 INTRODUCTION

In Chapter 2 the bridge-cleavage reactions of $[CODMCl]_2$ (M=Rh,Ir) with the 'metallo-ligands' (2), (6), (7) and (8) to form Pt(II)/Rh(I) and Pt(II)/Ir(I) hetero-metallic systems were described. In this chapter the bridge-cleavage reactions of $[(\eta^6\text{-arene})MCl_2]_2$ (M=Ru(II), Os(II)) and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (M=Rh(III),Ir(III)) with the full complement of chalcogenide 'metallo-ligands' produced by reaction of $Pt(S_2CNR_2)_2$ with $Ph_2P(E)H$ are described. As considerable synthetic use is made of the $[(arene)MCl_2]_2$ systems in this and subsequent chapters a brief description of some chemistry of these compounds is provided in Section 3.2.

3.2 CHEMISTRY OF $[(arene)MCl_2]_2$ (M=Ru,Os)

The dichloro-bridged, binuclear complexes $[(arene)MCl_2]_2$ ((69) M=Ru, arene=C_6H_6,p-cymene, C_6Me_6; (70) M=Os, arene=C_6H_6, p-cymene) have been the subject of extensive studies over the past fifteen years.[139-142]



(69) M=Ru

(70) M=Os

Their dimeric nature has been established by molecular-weight measurements and unequivocally confirmed for $[(p\text{-cym})OsCl_2]_2$ (70) by an X-ray structure determination[143]. The synthetic utility of (69) and (70) for the production of derivatives containing the $M(II)(arene)^{2+}$ fragment is considerable[144,145]. A characteristic reaction, in common with the $[CODMCl]_2$ systems of Chapter 2, is that of bridge cleavage with a variety of Lewis bases to yield monomeric products.

The product of the reaction of $[(arene)MCl_2]_2$ (M=Ru,Os) with a monodentate ligand (L) is dependent on the reaction-solvent polarity. In non-polar solvents reaction with excess (L) generates a neutral product, while in polar solvents a monocationic product is formed [Equations 36 and 37].

$$[(arene)MCl_2]_2 \xrightarrow[\text{non-polar solvent}]{\text{Excess L}} 2[(arene)MCl_2L] \quad \ldots [36]$$

M=Ru, L=PR_3, $P(OR)_3$, AsR_3, SbR_3, dmso, py, SEt_2, dppm, CO [139,140,146]
M=Os, L=PR_3, $P(OR)_3$, $CNCMe_3$, dmso, CO [142]

$$[(arene)MCl_2]_2 \xrightarrow[\text{polar solvent}]{\text{Excess L}} 2[(arene)MClL_2]^+ \quad \ldots [37]$$

M=Ru, L=PR_3, $AsPh_3$, SEt_2, NH_3, MeCN, py [141,146,147]
M=Os, L=py [141]

An extensive range of mixed-ligand complexes of the type $[(arene)RuCl(L)(L')]PF_6$ (arene=C_6H_6, L=PPh_3, L'=PMe_3, PMe_2Ph, $PMePh_2$; L=$OCMe_2$, L'=PMe_3, PMe_2Ph, PPh_3; L=C_2H_4, L'=PMe_3;

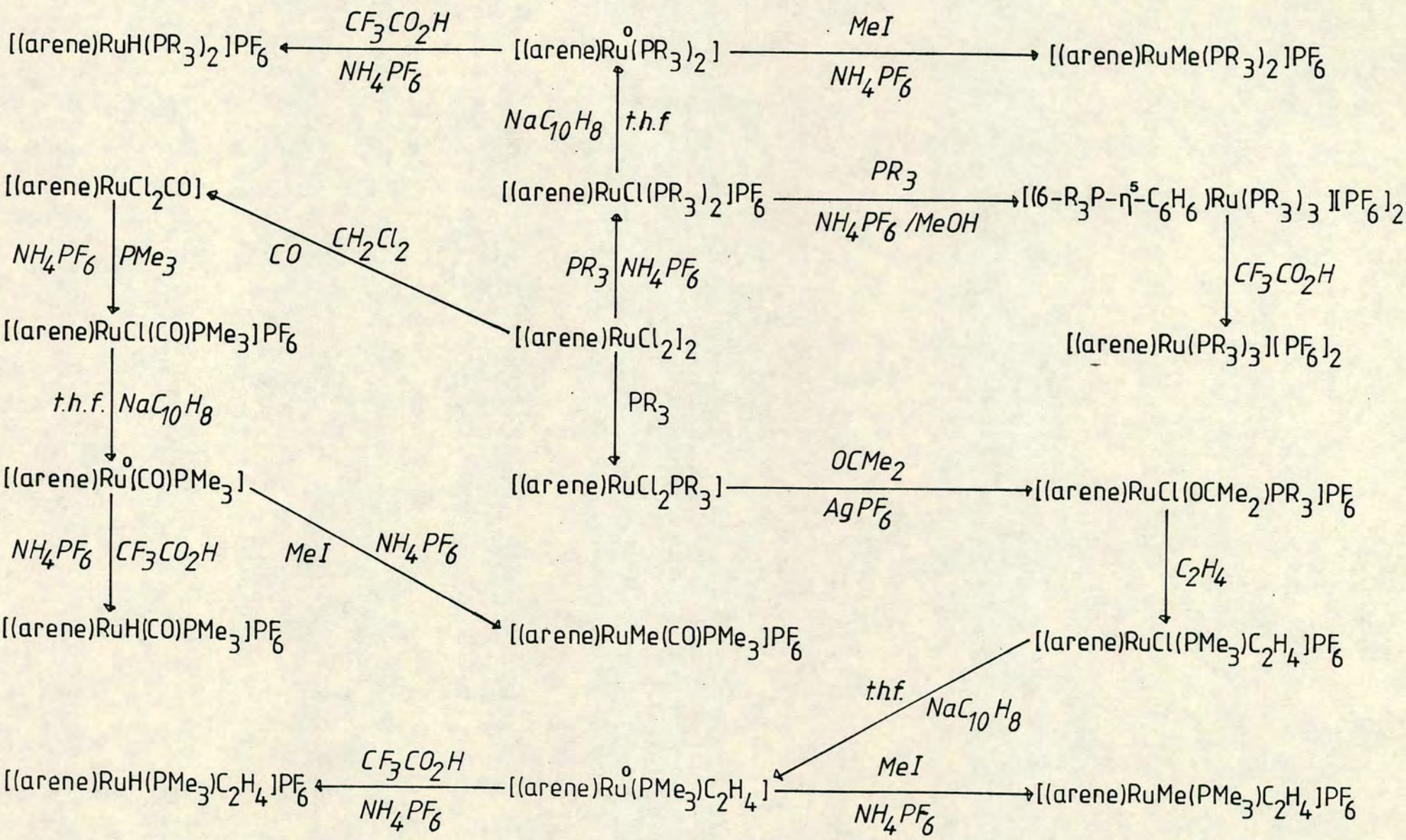
arene=p-cymene, C_6Me_6, L=CO,L'=PMe_3) have been reported by Werner[148,149]. Several of the mixed-ligand complexes undergo a $2e^-$ reduction with $NaC_{10}H_8$ to produce reactive, electron-rich Ru(O) species [Equation 38] [150]. The complexes [(arene)Ru(L)(L')] can then react with either MeI or CH_3COOH in the presence of NH_4PF_6 to give derivatives of the type [(arene)Ru(L)(L')R]PF_6 (R=Me,H). The alkene ligand in [(C_6H_6)Ru$(PMe_3)(CH_2CH_2)$H]PF_6 undergoes a facile ethene/ethyl interconversion [Equation 39] and in [(arene)Ru(PMe_3)-(CH_2CH_2)Me]PF_6 is highly electrophilic and readily forms phosphorus ylide moieties [Equation 40]. A summary of work in this area is given for Ru in Scheme 9 and Os in Scheme 10 [144, 149,150].

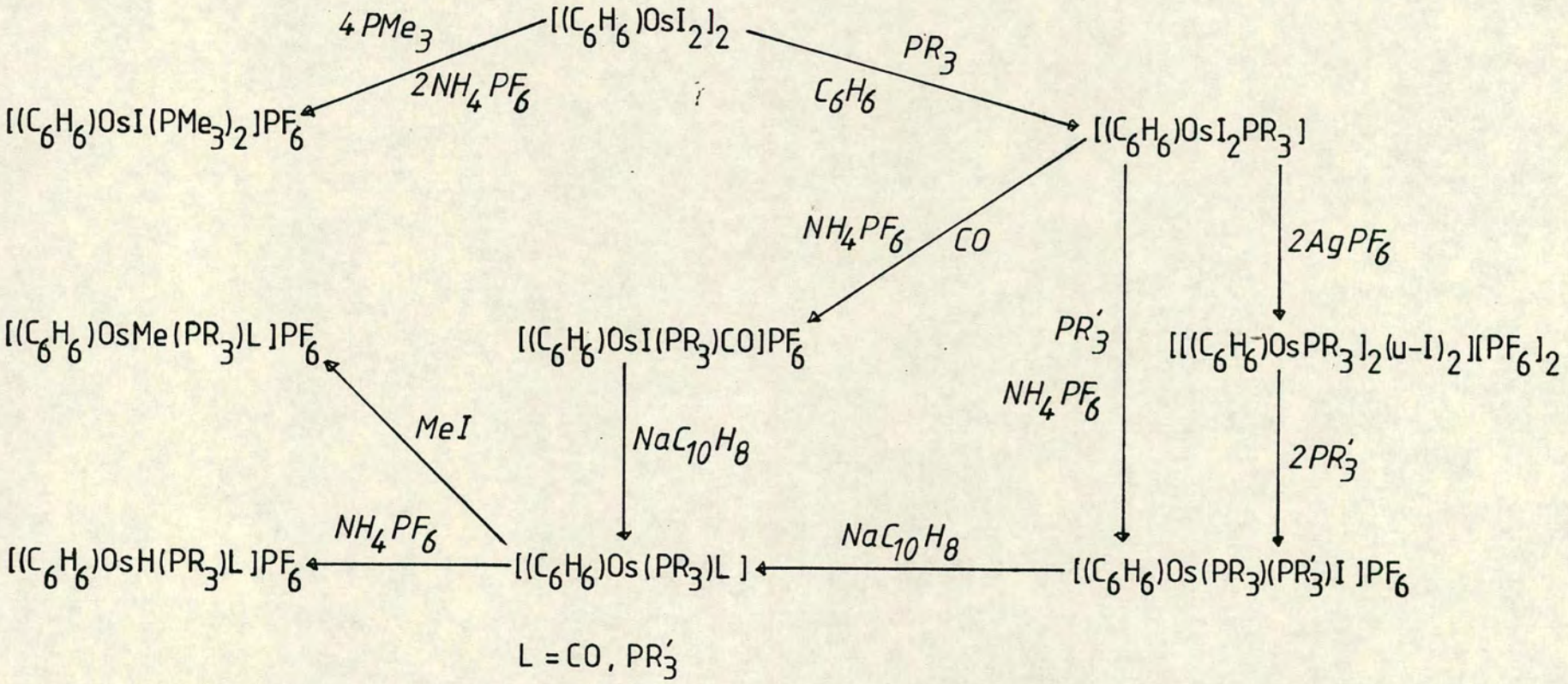
$$[(\text{arene})\text{RuCl}(\text{L})(\text{L}')]PF_6 \xrightarrow[\text{t.h.f. } -78^\circ C]{2NaC_{10}H_8} [(\text{arene})\overset{\circ}{\text{Ru}}(\text{L})(\text{L}')] + 2C_{10}H_8 + NaCl + NaPF_6 \quad \ldots\ldots [38]$$

$$[(C_6H_6)\text{Ru}(PMe_3)(CH_2CH_2)\text{H}]^+ \xrightarrow{PMe_3} [(\text{arene})\text{Ru}(PMe_3)_2\text{Et}]^+ \xrightarrow{[CPh_3][PF_6]} [(\text{arene})\text{Ru}(PMe_3)_2(CH_2CH_2)]^{2+} \quad \ldots\ldots [39]$$

$$[(\text{arene})\text{Ru}(PMe_3)(CH_2CH_2)\text{Me}]^+ \xrightarrow{PMe_3} [(\text{arene})\text{Ru}(PMe_3)(C_2H_4PMe_3)\text{Me}]^+ \quad \ldots\ldots [40]$$

Scheme 9: Chemistry of complexes of the type $[(arene)Ru(L)(L')Cl]PF_6$



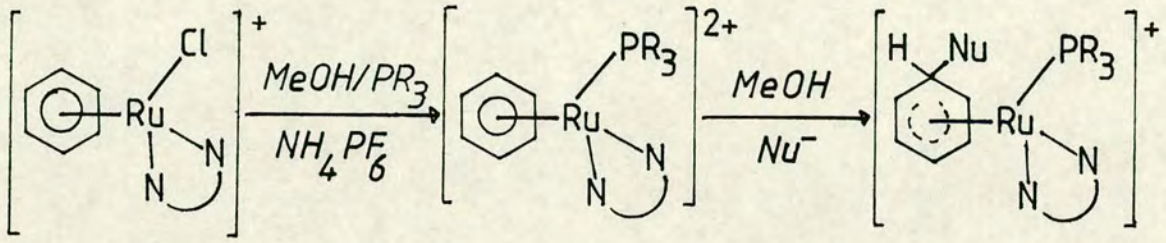


Scheme 10: Chemistry of the complex $[(arene)OsI_2]_2$

Neutral derivatives of the type $[(C_6H_6)Ru(PR'_3)R(Cl)]$ (R=Me,Ph) have been prepared by reaction of $[(C_6H_6)RuCl_2]_2$ with the alkylating agents $HgMe_2$, $SnMe_4$ or $HgPh_2$ in acetonitrile followed by treatment with a tertiary phosphine [140]. Similarly, complexes of the type [(p-cym)Os(L)Me(Cl)] are formed either by reaction of Al_2Me_6 with $[(p\text{-cym})OsCl_2L]$ (L=CO, dmso, $CNCMe_3$, PMe_3) in toluene or for L=PPh_3, $P(OPh)_3$ by displacement of dmso from the complex [(p-cym)Os(dmso)Me(Cl)]. The attempted preparation of [(p-cym)Os(L)Me(Cl)] for L=PPh_3 and $P(OPh)_3$ using Al_2Me_2 and $[(p\text{-cym})OsCl_2L]$ yielded ortho-metallated products[142]. A number of complexes of the type $[(arene)RuL_3]^{2+}$ have been prepared (L=PR_3 (Scheme 9), MeCN, N_2H_4, NH_2NMe_2, py, NH_3, $OCMe_2$) [140,155-157]. These are generally generated by reaction of the ligand L with $[(arene)RuCl_2]_2$ in the presence of $NaBPh_4$, NH_4PF_6, $AgBF_4$ or $AgPF_6$ in a polar solvent.

The reaction of $[(C_6H_6)RuCl_2]_2$ with neutral, bidentate ligands $\overset{\frown}{L}$ ($\overset{\frown}{L}$=1,10-Phen, bipy, dppe, dppp, dppb, dpae) can lead to the recovery of complexes of the type $[(C_6H_6)Ru(\overset{\frown}{L})Cl]Y$ containing the ligand chelate. When $[(C_6H_6)RuCl_2]_2$ is stirred in methanol with an excess of 1,10-phenanthroline for one hour the yellow,monocationic complex $[(C_6H_6)Ru(1,10\text{-Phen})Cl]PF_6$ can be isolated on NH_4PF_6 addition. Treatment with tertiary phosphines (not PPh_3 or dppe) yields the mixed amine/phosphine dicationic products $[(C_6H_6)Ru(1,10\text{-Phen})PR_3][PF_6]_2$. The arene ring in these dications is susceptible to attack by nucleophiles (Nu^-) to give air-stable, η^5-cyclohexadienyl complexes [Equation 41] [158,159]. Similarly, the diphosphines

$Ph_2P(CH_2)_nPPh_2$ (n=2-4) and dpae react with $[(C_6H_6)RuCl_2]_2$ in a 2:1 molar ratio in refluxing ethanol to give the monocationic chelates $[(C_6H_6)Ru(\overset{\frown}{L}\ \overset{\frown}{L})Cl]^+$, which may be isolated as either the chloride or tetraphenylborate salts[160].



$\overset{\frown}{N}\ \overset{\frown}{N}$=1,10-Phen; bipy. $PR_3 = PMe_2Ph, PEt_2Ph$ $Nu^- = H^-, OH^-, CN^-$

-------[41]

The reaction of $[(arene)RuCl_2]_2$ with the bidentate anionic ligands O_2CR^- (R=Me,CF_3) and $S_2PR_2^-$ (R=Me,Ph,OMe, OEt) gives two types of products depending on the reaction conditions and the ratio of reactants [Figure 15].

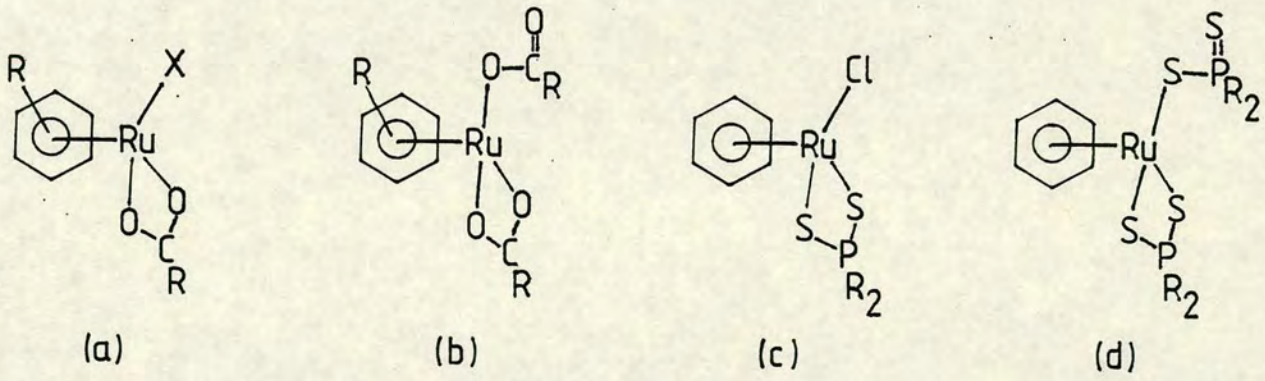
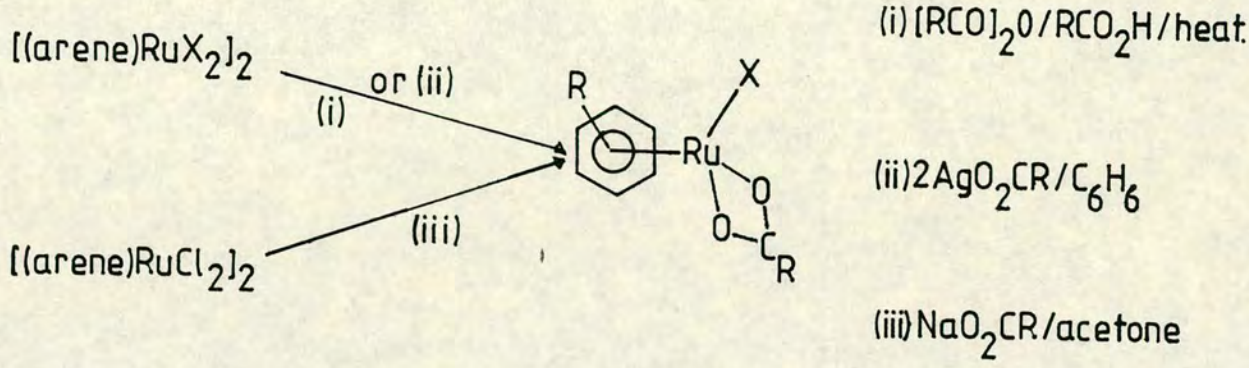


Figure 15: Products from the reaction of $[(arene)RuX_2]_2$ with $O_2CR_2^-$ and $S_2PR_2^-$ ligands.

Three methods have been developed for the preparation of complexes of type (a) in Figure 15 and these are given in Scheme 11 [161,162].



Scheme 11: Preparation of compounds of type (a) Figure 15 by various routes.

The bis(acetato) complex [(arene)Ru(O_2CR)$_2$] ((b) Figure 15, R=Me, all arenes) which contains uni- and bi-dentate bound acetate ligands can be prepared by the reaction of [(arene)$RuCl_2$]$_2$ with 4 molar equivalents of AgO_2CMe in benzene. These are converted to the corresponding bis(trifluoroacetates) ((b) Figure 15, R=CF_3), isolated as the monohydrates, by treatment with trifluoroacetic acid. Formation of [(arene)Ru(O_2CF_3)$_2$] directly by treatment of [(arene)$RuCl_2$]$_2$ with AgO_2CF_3 is only feasible for the benzene complex [162,163].

The complexes [(arene)Ru(O_2CR)Cl] and [(arene)Ru(O_2CR)$_2$] are useful synthetic precursors owing to the lability of the carboxylate ligand. Treatment of [(C_6H_6)Ru(O_2CF_3)Cl] with L (L=py (neat), PPh_2Et (neat), L_2=bipy in MeOH) provides an alternative route to the monocationic complexes [(C_6H_6)RuL_2Cl]$^+$ [141,146,159], while reaction in methanol with an excess of pyrazine, a potential binucleating ligand, (also 4,4-bipy and 1,3-dithiane) produces the new species

$[(C_6H_6)Ru(pyz)_2Cl]^+$, which can be isolated as a PF_6^- salt. The single crystal X-ray structure of $[(p\text{-cym})Ru(pyz)_2Cl]PF_6$, formed directly by reaction of $[(p\text{-cym})RuCl_2]_2$ and pyrazine in methanol in the presence of NH_4PF_6, reveals the uncoordinated ring-nitrogens to be too far apart for efficient bidentate coordination of an additional metal[162].

Reaction of $[(C_6Me_6)Ru(O_2CR)_2]$ (R=Me,CF_3) with PPh_3 in benzene affords the phosphine adduct $[(C_6Me_6)Ru(O_2CR)_2PPh_3]$ in which both carboxylate ligands assume monodentate coordination[162]. Alternative routes to the complexes $[(C_6Me_6)Ru(O_2CR)_2PR_3]$ (PR_3=PMe_3, $PMePh_2$, PPh_3, R=CF_3 [164]; PR_3=PMe_3, R=Me[165]) involve either the stepwise rupture of Ru-C bonds in $[(C_6Me_6)Ru(PR_3)Me_2]$ with CF_3COOH or the reaction of AgO_2CMe with $[(C_6Me_6)RuCl_2(PMe_3)]$.

The reaction of $[(arene)RuCl_2]_2$ with simple dithio-acid ligands is only successful for a series of dithiophosphinates $S_2PR_2^-$ (R=Me, Ph, OMe, OEt). The red crystalline solids recovered from the reaction of $[(C_6H_6)RuCl_2]_2$ with excess of NaS_2PR_2 in water have been characterised by a range of techniques and formulated as the neutral monomeric species $[(C_6H_6)Ru(S_2PR_2)_2]$ ((d) Figure 15). The mono- and bi-dentate bound dithio ligands retain stereo-chemical integrity before product decomposition occurs at elevated temperature. Under more controlled conditions, the reaction of $[(C_6H_6)RuCl_2]_2$ with two molar equivalents of $NH_4S_2PPh_2$ in methanol, produces the complex $[(C_6H_6)Ru(S_2PPh_2)Cl]$ ((c) Figure 15). In contrast, the reaction of either dithio-carbamates ($S_2CNR_2^-$) or dithiocarbonates (S_2COR^-) with

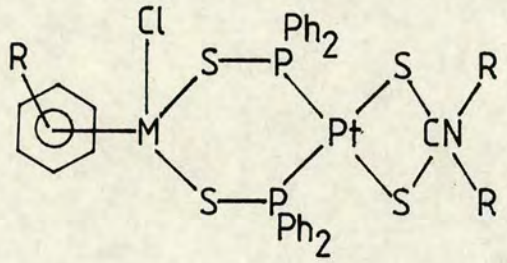
$[(arene)RuCl_2]_2$ leads to loss of the arene ring and the formation of paramagnetic species. A series of derivatives of the type $[(C_6H_6)Ru(S_2PPh_2)L]PF_6$ can be prepared by treatment of $[(C_6H_6)Ru(S_2PPh_2)Cl]$ with various Lewis bases L ($L=PPh_3$, $PMePh_2$, $P(OMe)_3$, py, $AsPh_3$, $SbPh_3$) in ethanolic NH_4PF_6 [158,166,167].

Reaction of the neutral macrocyclic ligands 1,4,7-trithiacyclononane and 1,4,7-triazacyclononane (L^1) with $[(arene)MCl_2]_2$ (M=Ru,arene=C_6H_6, p-cymene; M=Os, arene=p-cymene) gives the mixed-ligand complexes $[(arene)M(L^1)]^{2+}$, while reaction of the 1,4,7,10,13,16-hexathiacyclooctadecane (L^2) ligand produces the bimetallic complex $[M_2Cl_2(arene)_2(L^2)]^{2+}$ with each metal ion bound to two sulphur atoms of the macrocycle to give a symmetrical structure[168]. The reaction of $[(arene)MCl_2]_2$ with $Tl(C_5H_5)$ provides a convenient high-yield preparation of mixed-sandwich cations $[M(arene)(C_5H_5)]^+$ (M=Ru, arene=C_6H_6, p-cym, C_6H_5OMe, C_6Me_6; M=Os, arene=C_6H_6, p-cym)[169,170]. Finally $[(arene)RuCl_2]_2$ can also be used for the preparation of a wide range of homo-binuclear bridged cations of the type $[Ru_2X_3(arene)_2]^+$ (X=Cl, Br, I, OH, OR, SR) [141,146,171], $[Ru_2HXY(arene)_2]^+$ (X=Y=Cl, OCOR; X=Cl, Y=OCOR; R=Me, CF_3) [172] and also homo-tetranuclear cations such as $[(C_6H_6)Ru(OH)]_4^{4+}$ [173] and $[(C_6H_6)_4Ru_4(\mu_2\text{-}OH)(\mu_4\text{-}O)]^{2+}$ [174].

3.3.1 REACTION OF $[NH_2R_2][Pt(S_2CNR_2)(Ph_2PS)_2]$ WITH $[(\eta^6\text{-arene})MCl_2]_2$ (M=Ru, arene=C_6H_6, p-cymene, C_6Me_6; M=Os, arene=p-cymene)

After stirring a 2:1 molar ratio of $[NH_2Et_2]$-$[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (6) and $[(C_6H_6)RuCl_2]_2$ in chloroform for 15 minutes a bright-red product can be precipitated on addition of methanol. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the product run in $CDCl_3$ reveals a single 1:4:1 triplet resonance at δP 37.8 p.p.m. with $^1J_{PtP}$ 3461.9Hz. The magnitude of the $^1J_{PtP}$ coupling constant suggests that the Pt-P linkages remain intact and the simple spectrum indicates that the P-atoms, in the only P-containing product, are equivalent. The ^1H n.m.r. spectrum of the product shows a singlet resonance at 5.4 p.p.m. which is in the region appropriate for benzene π-bonded to Ru. Triplet (δ_{CH_3} 1.17 p.p.m.) and quartet (δ_{CH_2} 3.51 p.p.m.) resonances are observed for the ethyl groups of the dithiocarbamate ligand; resonances for the phenyl rings of the bridging P atoms occur between 7 and 8 p.p.m. Integration of the spectrum shows that one C_6H_6 ring is present for each $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ unit in the product. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum reveals four non-phenyl carbon environments. The signals at δ_C 44.0, 12.2 and 204.9 p.p.m. can be assigned to δ_{CH_2}, δ_{CH_3} and δ_{CN} respectively for the dithiocarbamate ligand and the remaining intense signal at 85.6 p.p.m. to the benzene carbons. The i.r. spectrum shows ν_{CN}=1525 cm^{-1} and ν_{PS}=584 cm^{-1} but does not contain a band assignable to a terminal Ru-Cl stretching vibration. However, the non-

electrolytic behaviour of the product in acetone and methylene chloride suggests a further anionic ligand (chloride) is coordinated at the ruthenium ion to sustain neutrality. With favourable analytical data the available evidence suggests the formulation of the product as the neutral dibridged heterobimetallic $[(C_6H_6)RuCl(\mu\text{-}SPPh_2)_2\text{-}Pt(S_2CNEt_2)]$ (71) derived from simple bridge-cleavage of $[(C_6H_6)RuCl_2]_2$ by the anionic platinum-ligand (6).



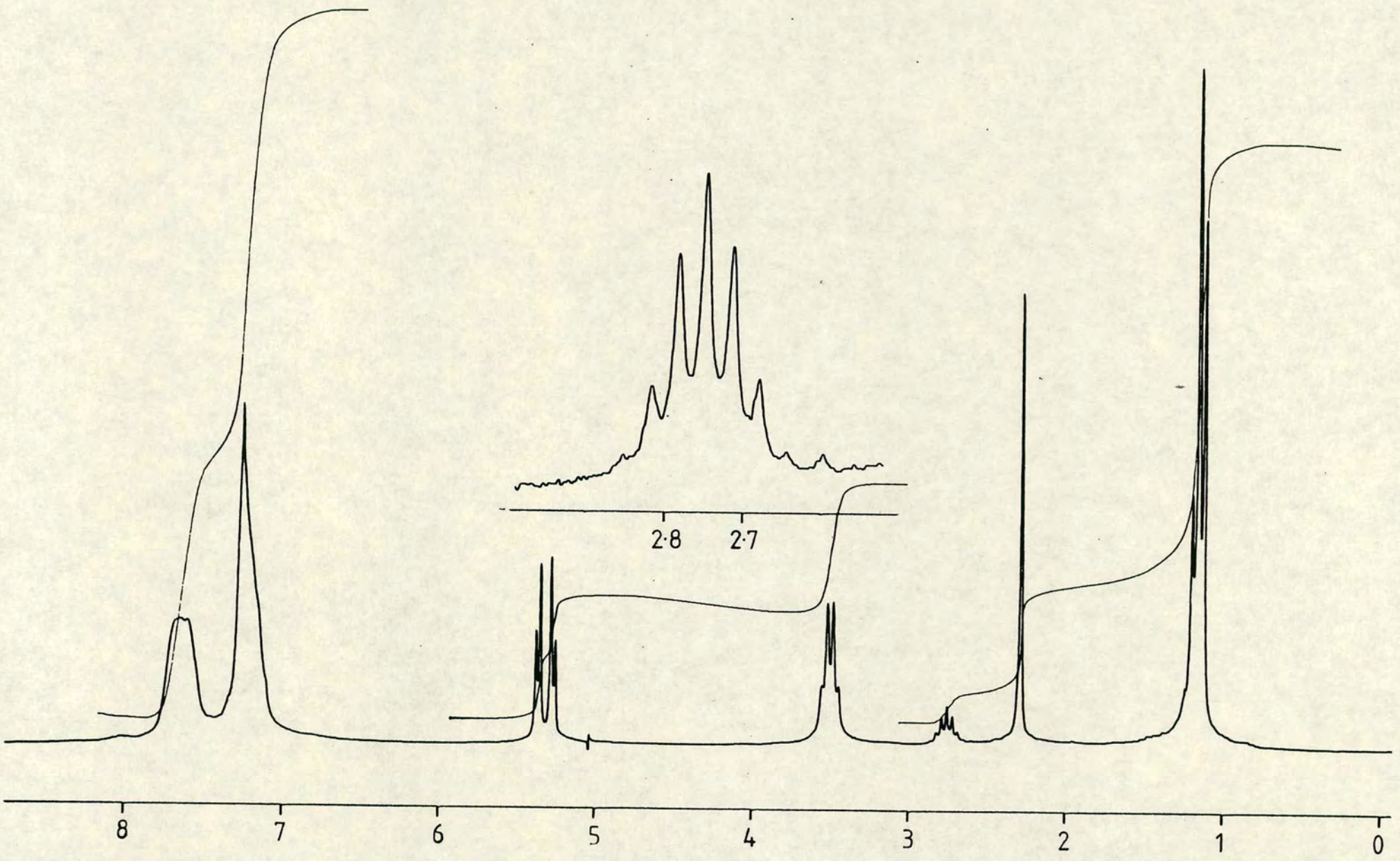
	M	arene	R		M	arene	R
(71)	Ru	C_6H_6	Et	(74)	Ru	p-cymene	^1Pr
(72)	Ru	p-cymene	Et	(75)	Ru	C_6Me_6	^1Pr
(73)	Ru	C_6H_6	^1Pr	(76)	Os	p-cymene	Et

Preparation of heterobimetallics with other arene rings bound at ruthenium is achieved by the equally facile reaction of $[NH_2R_2][Pt(S_2CNR_2)(Ph_2PS)_2]$ (R=Et, ^1Pr) with either $[(p\text{-cymene})RuCl_2]_2$ or $[(C_6Me_6)RuCl_2]_2$ in a 2:1 molar ratio to produce $[(p\text{-cym})RuCl(\mu\text{-}SPPh_2)_2Pt(S_2CNR_2)]$ ((72) R=Et; (74) R=^1Pr) and $[(C_6Me_6)RuCl(\mu\text{-}SPPh_2)_2Pt(S_2CN^1Pr_2)]$ (75). Characterisation of these complexes also relies heavily on spectroscopic results. All provide single 1.4.1 triplet resonances in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra and ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. studies supply assignment for the organic

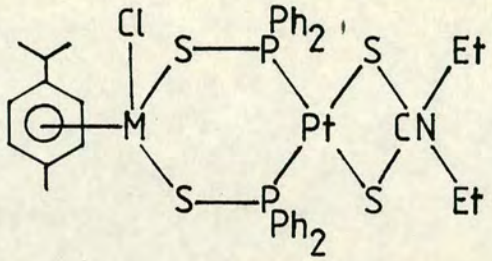
fragments in the molecules. The equimolar reaction of $[NH_2R_2][Pt(S_2CNR_2)(Ph_2PS)_2]$ (R=Et, ^1Pr) and $[(p\text{-cym})Ru(O_2CMe)Cl]$ in chloroform provides an alternative high yield route to the heterobimetallics (72) and (74). A large variation in δP is observed for the series. $[(arene)RuCl(SPPh_2)_2Pt(S_2CN^1Pr_2)]$ ((73) C_6H_6, δP 38.3 p.p.m.; (74) p-cymene, δP 34.9 p.p.m.; (75) C_6Me_6, δP 24.8 p.p.m.) and this may relate to the electron-donating ability of the arene ring.

The yellow heterobimetallic complex $[(p\text{-cym})OsCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (76) can be prepared in the 2:1 molar reaction of (6, R=Et) with the chloroform-soluble complex $[(p\text{-cym})OsCl_2]_2$. As anticipated, the i.r., ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra for the complexes (72) and (76) are very similar, with the M(II) ion influencing the observed signal position for comparable molecular fragments. The ^1H n.m.r. spectrum of (76) [Figure 16] shows signals for the p-cymene ring ($\delta_{C\underline{H}_3}$ 2.27 p.p.m. singlet; $\delta_{C\underline{H}Me_2}$ 2.75 p.p.m. septet, $\delta_{CH(C\underline{H}_3)_2}$ 1.13 p.p.m. doublet; arene protons 5.3 p.p.m. AB resonance), the diethyldithiocarbamate ligand ($\delta_{C\underline{H}_2}$ 3.49 p.p.m. quartet; $\delta_{C\underline{H}_3}$ 1.16 p.p.m. triplet) and the phenyl-group protons of the bridging P atoms ($\delta_{C_5\underline{H}_6}$ 7-8 p.p.m.). In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (76) ten non-phenyl carbon resonances appear as required for the proposed structure which can be assigned on the basis of an EPT experiment and by comparison with data from related systems. The i.r. spectrum shows ν_{CN}=1515, ν_{PS}=590 cm^{-1} and a weak band at 282 cm^{-1} which is assigned to the terminal ν_{OsCl}

Figure 16: The ^{1}H n.m.r. spectrum of [(p-cymene)OsCl(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (76) in $CDCl_3$ at 293°K



stretching vibration. $^{31}P-\{^{1}H\}$ n.m.r. data (1:4:1 triplet δP 28.4 p.p.m., $^{1}J_{PtP}$ 3464.3Hz), microanalysis results and the non-electrolytic behaviour in acetone and chloroform confirm assignment of the product (76).



(72) M=Ru

(76) M=Os

The heterobimetallics (71-76) are air-stable solids which decompose when heated to above 200°C in air. They are soluble and stable for extended periods in chlorinated hydrocarbons and are insoluble in alcohols, ethers, hydrocarbons and nitromethane.

3.3.2 DERIVATIVES OF THE HETEROBIMETALLICS [(arene)MCl-(μ-SPPh$_2$)$_2$Pt(S$_2$CNR$_2$)] (71-76)

Investigations were directed toward replacement of the ruthenium or osmium-bound, terminal chloride by a variety of neutral ligands (L) to yield monocationic complexes of the type $[(arene)ML(\mu\text{-}SPPh_2)_2Pt(S_2CNR_2)]^+$. Two methods were identified for the synthesis of such derivatives [Methods A and B, Equation 42]. In most cases one of the methods proved superior and in some cases necessary for the preparation of a given derivative.

$[(arene)MCl(SPPh_2)_2Pt(S_2CNR_2)]$ METHOD A

$-Cl^-$ | L

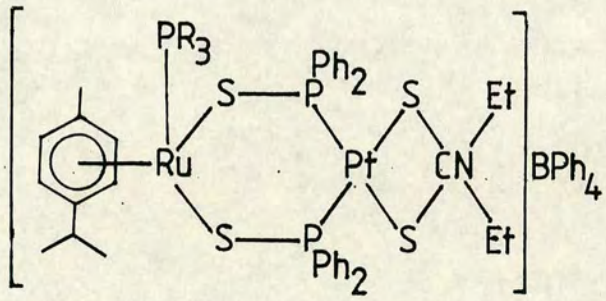
$[(arene)ML(SPPh_2)_2Pt(S_2CNR_2)]^+$ ... [42]

$-2Cl^-$ ↑

$[(arene)MCl_2L]+[Pt(S_2CNR_2)(Ph_2PS)_2]^-$ METHOD B

REACTION OF HETEROBIMETALLICS (71-76) WITH MONODENTATE AND BIDENTATE LIGANDS

3.3.3 TERTIARY PHOSPHINE DERIVATIVES (M=Ru ONLY)



	arene	PR_3-
(77)	C_6H_6	PPh_2Et
(78)	p-cym	PPh_2Et
(79)	p-cym	PPh_3

Both methods are successful for the preparation of tertiary phosphine derivatives. No reaction occurs when an equimolar quantity of $[(C_6H_6)RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (71) and PPh_2Et are stirred in chloroform at ambient temperature for 3 hours. If however the solution is refluxed for 4 hours a darkening of the original red colour can be detected. Concentration of the reaction solution followed by addition of methanolic $NaBPh_4$ precipitates a

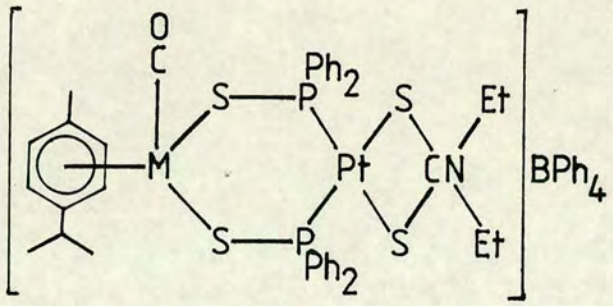
brown solid which can be recovered as an air-stable product. The ^{1}H n.m.r. spectrum of the product confirms that the benzene ring remains coordinated and unchanged at ruthenium with the appearance of a singlet resonance at 5.12 p.p.m. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum [Figure 17] supplies cogent evidence that during reaction the terminal chloride is replaced by PPh_2Et. A 1:4:1 triplet (δP 44.5 p.p.m., $^{1}J_{PtP}$ 3409.4Hz) of doublets ($^{3}J_{PP}$ 16.9Hz) resonance appears for the bridging phosphorus atoms with the doublet splitting derived from three-bond coupling to the P atom bound to Ru. The Ru-bound P atom appears as a triplet resonance (δP 30.2 p.p.m.) due to coupling to the two equivalent bridging P atoms. The information available from this spectrum is sufficient to define the $\overline{PRuSPPtPS}$ core. All other evidence (i.r. spectrum ν_{CN}=1525, ν_{PS}=594 cm^{-1}, solution conductivity and microanalytical data) is consistent with formulating the brown product as the monocationic, tertiary phosphine complex $[(C_6H_6)Ru(PPh_2Et)(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (77). The complex $[(p\text{-}cym)Ru(PPh_2Et)(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (78) was also prepared by Method A.

Method B was used to prepare the complex $[(p\text{-}cym)Ru(PPh_3)(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (79) and involved refluxing an equimolar quantity of (6, R=Et) and $[(p\text{-}cym)RuCl_2(PPh_3)]$ in chloroform for 5 hours followed by addition of methanolic $NaBPh_4$ to precipitate the brown product.

Without doubt Os/Pt heterobimetallics of the type

$[(arene)Os(PR_3)(\mu\text{-}SPPh_2)_2Pt(S_2CNR_2)]^+$ could be prepared by either preparative method. Attempts to produce Rh/Pt heterobimetallics of the type $[(C_5Me_5)Rh(PR_3)(\mu\text{-}SPPh_2)_2\text{-}Pt(S_2CNR_2)]^+$ by Method A were unsuccessful with breakdown of the bimetallic unit observed. The Pt monometallic decomposition product was idehtified by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy as the complex $[Pt(S_2CNR_2)(Ph_2PS)(PEt_3)]$. (See also Section 5.6).

3.3.4 MONOCARBONYL DERIVATIVES



	M
(80)	Ru
(81)	Os

Attempts to prepare the monocarbonyl derivatives $[(arene)RuCO(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (arene=C_6H_6, p-cymene (80)) by either Method A or B were not wholly successful. Treatment of $[(C_6H_6)RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (71) with CO in $CDCl_3$ for 10 minutes resulted in the loss of the benzene ring (^1H n.m.r. evidence) and the generation of several unidentified species ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence) likely to contain CO (i.r., ν_{CO} several bands 2060-1940 cm^{-1}).

The equimolar reaction of (6, R=Et) and $[(p\text{-cym})\text{-}RuCl_2CO]$ proceeds rapidly at room temperature in $CDCl_3$ to

produce a major species, which reveals a 1:4:1 triplet resonance (δP 30.3 p.p.m., $^{1}J_{PtP}$ 3386.2Hz) in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum. The ^{1}H n.m.r. spectrum of the reaction solution confirms that the p-cymene ring remains coordinated. A sharp band at 2015 cm^{-1} corresponding to a ν_{CO} stretching vibration is detected in the i.r. spectrum of the brown solid recovered on addition of methanolic $NaBPh_4$ to the reaction solution (also ν_{CN}=1524, ν_{PS} 588 cm^{-1}). On this evidence the formation of $[(p\text{-cym})Ru(CO)(SPPh_2)_2Pt(S_2CNEt_2)]^+$ (80) as the major reaction product is proposed. The monomeric complex $[(C_6H_6)RuCl_2CO]$ has a transient existence in solution[139] but $[(C_6Me_6)RuCl_2CO]$ can be isolated as a stable solid[148]. By analogy, the arene ring on the heterobimetallic must play an important role in stabilising the monocarbonyl derivative. It is anticipated that the formation of $[(C_6Me_6)Ru(CO)(SPPh_2)_2Pt(S_2CNR_2)]^+$ would be successful using either Method A or B.

When $[(p\text{-cym})OsCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (76) is treated with CO in $CDCl_3$ a slow quantitative conversion to the monocarbonyl complex $[(p\text{-cym})Os(CO)(SPPh_2)_2Pt(S_2CNEt_2)]^+$ (81) is observed. In situ $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy shows that the 1:4:1 triplet resonance for (76) (δP 28.7 p.p.m., $^{1}J_{PtP}$ 3459.4Hz) is gradually replaced over a 4 minute period by a similar resonance for (81) (δP 27.0 p.p.m., $^{1}J_{PtP}$ 3371.6 Hz). The product can be recovered from the reaction solution, on addition of methanolic $NaBPh_4$, as a yellow solid. The i.r. spectrum of the isolated product (81) shows a single ν_{CO} stretching vibration at 1995 cm^{-1}, with ν_{CN}=1528 and ν_{PS}=586

cm^{-1} also detected. In the ^1H n.m.r. spectrum, signals for the p-cymene ring and the ethyl groups of the dithiocarbamate are detected with the correct integration for (81). The spectrum also revealed some residual methanol in the product which is thought to be responsible for the low microanalysis values for C, H and N obtained for (81).

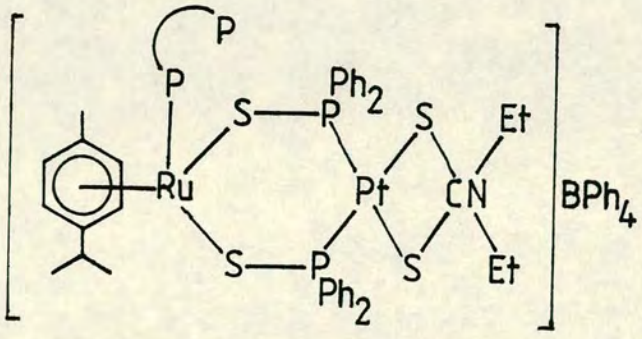
3.3.5 ACETYLENIC DERIVATIVES

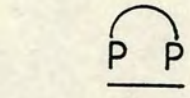
A slow room-temperature reaction occurs on treating [(p-cym)OsCl(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (76) with excess phenylacetylene in $CDCl_3$. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the reaction solution reveals that over a 10 minute period the 1:4:1 triplet resonance for (76) is slowly replaced by a similar resonance at lower frequency (δP 26.8 p.p.m., $^1J_{PtP}$ 3374.0Hz). The i.r. spectrum of the brown product, precipitated from the reaction solution on addition of methanolic $NaBPh_4$, shows a strong band at 2000 cm^{-1} which is attributed to a $\nu_{C\equiv C}$ stretching vibration (also ν_{CN}=1518 and ν_{PS} 578 cm^{-1}). ^1H n.m.r. and analytical data indicate that the product is isolated with contaminants. However on the evidence available the formation of the acetylenic complex [(p-cym)Os(PhCCH)(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)]BPh$_4$ (82) is proposed. No reaction occurred on treating [(p-cym)RuCl(SPPh$_2$)$_2$Pt-(S$_2$CNEt$_2$)] (72) with an excess of PhCCH even under refluxing conditions.

3.3.6 ALKENYL PHOSPHINE DERIVATIVES

The equimolar reaction of $[(p\text{-cym})RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (72) and the alkenyl phosphine $Ph_2P(CH_2)_2CHCH_2$ proceeds rapidly at room temperature in $CDCl_3$. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the product consists of a 1:4:1 triplet (δP 43.4 p.p.m., $^1J_{PtP}$ 3361.8Hz) of doublet ($^3J_{PP}$ 14.6Hz) resonance and a triplet (δP 26.6 p.p.m.) resonance similar to that obtained for the tertiary phosphine derivatives (77-79). This suggests that coordination of the alkenyl phosphine occurs through the phosphorus atom to give the cation $[(p\text{-cym})Ru(\underline{P}\text{-}Ph_2P(CH_2)_2CHCH_2)(SPPh_2)_2Pt(S_2CNEt_2)]^+$ (83), which can be isolated as a BPh_4^- salt on addition of methanolic $NaBPh_4$ to the reaction solution. The i.r. spectrum of the isolated product shows ν_{CN}=1525 and ν_{PS}=575 cm^{-1}. No evidence was obtained for a $\nu_{C=C}$ stretching vibration, although this vibration is often weak in complexes containing the alkenyl phosphine moiety[175].

3.3.7 DIPHOSPHINE DERIVATIVES





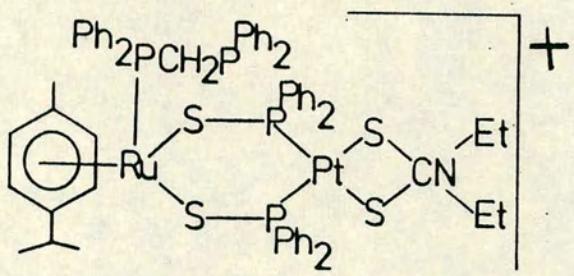
(84) dppm

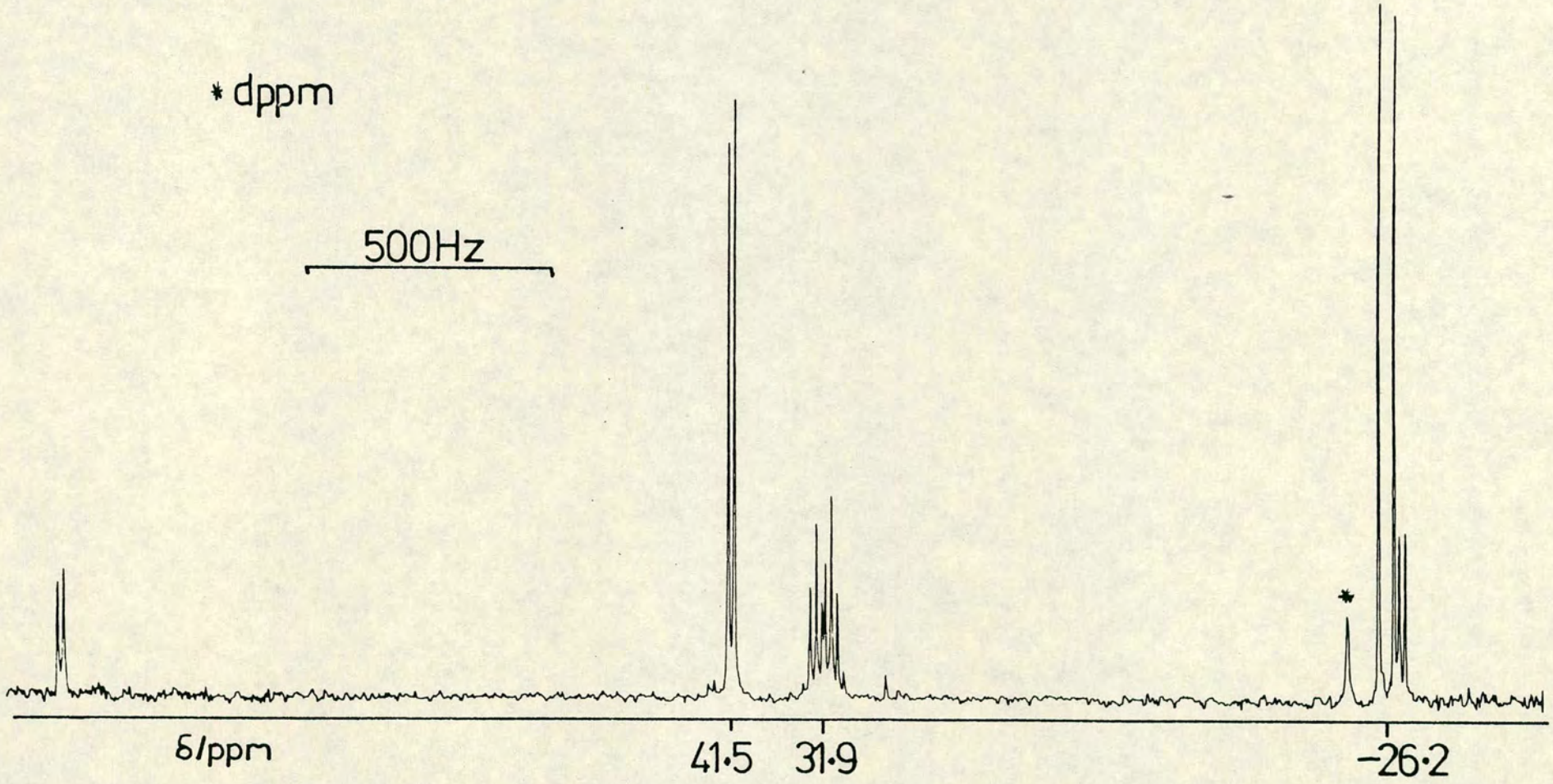
(85) dppe

The diphosphines $Ph_2PCH_2PPh_2$(dppm) and $Ph_2P(CH_2)_2$-PPh_2(dppe) react rapidly with an equimolar quantity of the heterobimetallic complex [(p-cym)RuCl$(SPPh_2)_2$Pt(S_2CNEt_2)] in chloroform at room temperature to yield, on addition of methanolic $NaBPh_4$, red products characterised as the novel species [(p-cym)Ru(diphosphine-P)$(SPPh_2)_2$Pt(S_2CNEt_2)]BPh_4 ((84) dppm, (85) dppe), which contain the diphosphine ligand bound in a monodentate fashion. The $^{31}P-\{^1H\}$ n.m.r. spectra for (84) [Figure 18] and (85) are very informative and only slightly more complex than the spectra for the mono-phosphine derivatives (77-79). The spectrum of (84) consists of three P resonances, which on the basis of chemical shift position and resonance multiplicity can be assigned to the two bridging P atoms (δP 41.5 p.p.m., 1:4:1 t of d, $^1J_{PtP}$ 3364.3Hz, $^3J_{PP}$ 14.7Hz); the Ru bound P (δP 31.9 p.p.m., d of t, $^2J_{PP}$ 38.1Hz) and the uncoordinated P atom of the dangling dppm ligand (δP -26.2 p.p.m., d). The spectrum for (85) is very similar with the resonance for the uncoordinated P atom of the dppe ligand appearing at δP -14.0 p.p.m. with $^3J_{PP}$ measured as 33.0Hz. The ^1H n.m.r. spectrum of (84) reveals signals in the correct ratio for the p-cymene ring, ethyl and phenyl groups and shows the methylene protons of the dppm ligand as a four-line resonance (δ_{CH_2} 3.32 p.p.m.).

This type of reaction can readily be extended to (76) and dppe to produce [(p-cym)Os(dppe-P)$(\mu$-$SPPh_2)_2$Pt(S_2CNEt_2)]-BPh_4. However, the equimolar reaction of (72) and $Ph_2As(CH_2)_2AsPh_2$(dpae) in $CDCl_3$ gives a mixture of the dangling and bridging dpae complexes

Figure 18: The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of [(p-cymene)Ru(dppm-P)$(SPPh_2)_2$Pt(S_2CNEt_2)]Cl (84) in $CDCl_3$ at 298°K



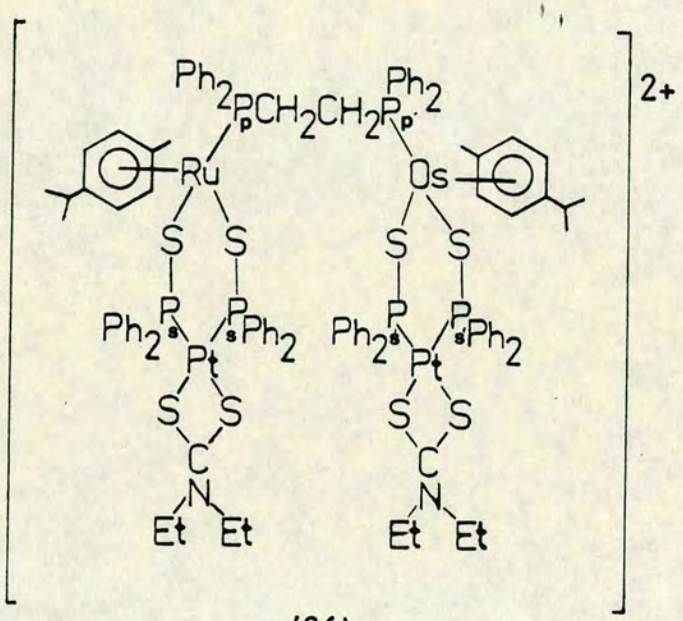


$[(p\text{-cym})Ru(dpae\text{-}As)(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]^+$ and $\{[(p\text{-cym})Ru(\mu\text{-}SPPh_2)_2Pt(S_2CNEt_2)]_2(\mu\text{-dpae})\}^{2+}$. Addition of a further quantity of (72) to the reaction mixture enables the bridged complex to be recovered as the only reaction product.

The reaction of a bidentate ligand to produce a complex in which the ligand has one donor atom bound to the metal and the remaining donor atom uncoordinated is of considerable synthetic value. It gives the opportunity to construct, in a controlled manner, heterometallic systems using the dangling donor atom as a site for binding an additional metal fragment. This concept is discussed fully in Chapters 4 and 5 with the inspiration for that work provided by the following study.

$[(p\text{-cym})Ru(dppe\text{-}P)(SPPh_2)_2Pt(S_2CNEt_2)]Cl$ was generated and characterised <u>in situ</u> by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. An equimolar quantity of $[(p\text{-cym})OsCl(SPPh_2)_2Pt(S_2CNEt_2)]$ was added to the reaction tube and the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum accumulated. The spectrum revealed four P environments. Notably, the doublet resonance assigned to the dangling P atom in (85) was not observed but was replaced by an overlapping doublet of triplets resonance (δP_P, -17.1 p.p.m.) in the region anticipated for P bound to Os. A related 1:4:1 triplet of doublets resonance appears at 45.0 p.p.m. and is assigned to the bridging phosphorus atoms (δP_S,) of the '$Os(SPPh_2)_2Pt$' unit. The signals for the '$RuP(SPPh_2)_2Pt$' unit remain as for (85) with only minor changes in the observed parameters (δP_S 46.8 p.p.m., t of d; δP_P 30.3 p.p.m., d of t) noted. The evidence clearly

supports the formation of the dppe-bridged heterotetrametallic (86). Microanalysis, i.r., ^{1}H n.m.r. and solution-conductivity data of the isolated bis[BPh_4^-] salt also confirm the rational synthesis of (86).



(86)

δP_s 46.8ppm $^1J_{PtP_s}$ 3370.9Hz

$\delta P_{s'}$ 45.0ppm $^1J_{PtP_{s'}}$ 3363.8Hz

δP_p 30.3ppm $^3J_{P_pP_s}$ 17.8Hz

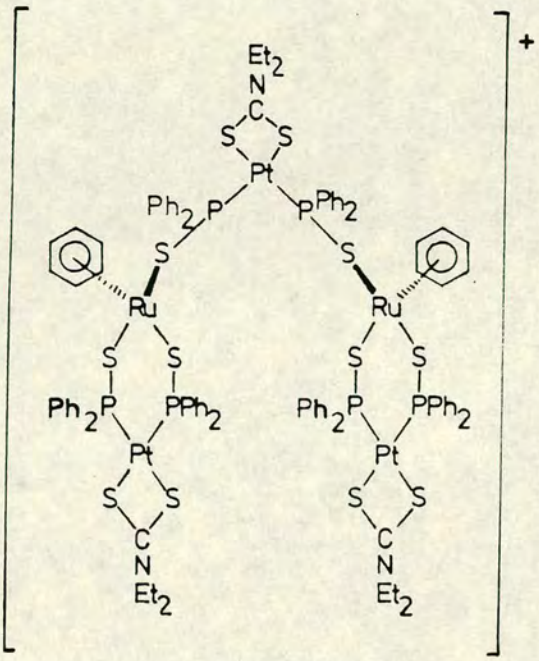
$\delta P_{p'}$ -17.1ppm $^3J_{P_pP_{s'}}$ 17.0Hz

$^3J_{P_pP_{p'}}$ 24.0Hz

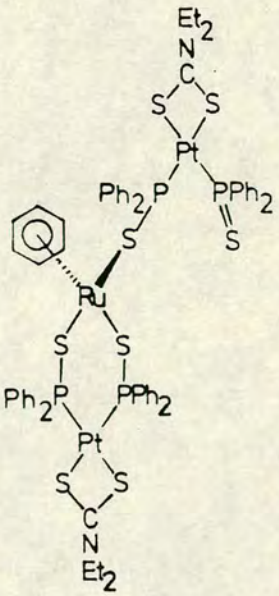
3.3.8 REACTION OF NEUTRAL HETEROMETALLICS WITH ANIONIC LIGANDS. REACTION OF [$(C_6H_6)RuCl(SPPh_2)_2Pt(S_2CNEt_2)$] (71) WITH (6, R=Et)

Preliminary investigations revealed that when $[(C_6H_6)RuCl_2]_2$ is treated with a ten-fold excess of $[Pt(S_2CNEt_2)(Ph_2PS)_2][NH_2Et_2]$ in $CDCl_3$ the neutral heterobimetallic (71) is only one of several species produced. In an attempt to identify the new species the heterobimetallic (71) was treated with approximately 0.5 molar equivalents of (6, R=Et) in $CDCl_3$. The *in situ*

$^{31}P-\{^{1}H\}$ n.m.r. spectrum of the reaction mixture showed three 1:4:1 triplet resonances, one of which could be assigned to (71) (δP 38.4 p.p.m., $^{1}J_{PtP}$ 3457.0Hz). The remaining two resonances (δP 39.7 p.p.m., $^{1}J_{PtP}$ 3432.6Hz; δP 34.8 p.p.m., $^{1}J_{PtP}$ 3366.7Hz) in a 2:1 ratio are consistent with the formation of the pentametallic species (87). After 20 minutes in solution the signals for (87) have diminished but the 2:1 ratio of intensity remains constant. The equimolar reaction of (71) and (6, Et) also produces the pentametallic species (87). In addition, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the reaction solution shows two related doublets (δP 36.2, 29.0 p.p.m., $^{2}J_{PtP}$ 19.5Hz) and a singlet (δP 38.9 p.p.m.) of low intensity (no Pt satellites observed) and is evidence for the dangling arrangement in the neutral, trimetallic complex (88). The doublets are no longer visible after 15 minutes but the signals for (87) appear to have grown at the expense of some previously unreacted (71). No further attempts were made to characterise (87) and (88).



(87)



(88)

3.3.9 REACTION OF [(arene)RuCl(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] WITH OTHER DITHIOACID SYSTEMS

When a methanolic suspension of [(p-cym)RuCl(SPPh$_2$)$_2$Pt-(S$_2$CNEt$_2$)] (72) is treated with an equimolar quantity of NaS$_2$PMe$_2$ a bright-red solid is deposited rapidly from the reaction solution in quantitative yield. The ^{31}P-{^{1}H} n.m.r. spectrum of the product in CDCl$_3$ shows a 1:4:1 triplet (δP 34.3 p.p.m., $^1J_{PtP}$ 3439.9Hz) and a singlet (δP 62.7 p.p.m.) resonance, which on a narrow spectral width reveal extra splittings with the 1:4:1 triplet showing a further doublet coupling and the singlet a triplet coupling measured as 0.5Hz ($^4J_{PP}$). This evidence suggests the formation of the product [(p-cym)Ru(S$_2$PMe$_2$)(SPPh$_2$)$_2$Pt-(S$_2$CNEt$_2$)] with the dithiophosphinate ligand bound in a monodentate fashion. Reaction of (72) with NaS$_2$CN^{i}Bu$_2$ in CDCl$_3$ gave the immediate formation of a dark green solution, which produced a silent ^{31}P-{^{1}H} n.m.r. spectrum. These observations are qualitatively similar to those reported by earlier workers for the successful preparation of bis-dithioacid complexes of the type [(C$_6$H$_6$)Ru(S$_2$PR$_2$)$_2$] [Figure 15(d)] and the unsuccessful reaction of NaS$_2$CNR$_2$ with [(arene)RuCl$_2$]$_2$ to give greenish-brown paramagnetic products[158,167].

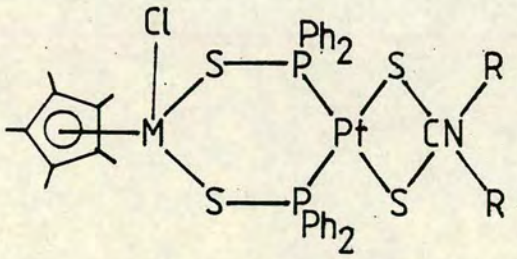
3.4.1 REACTION OF [NH$_2$R$_2$][Pt(S$_2$CNR$_2$)(Ph$_2$PS)$_2$] WITH [(η^5-C$_5$Me$_5$)MX$_2$]$_2$ (M=Rh, X=Cl,I; M=Ir, X=Cl)

Interest in the dichloro-bridged, binuclear complexes

$[(C_5Me_5)MCl_2]_2$ (M=Rh(III), Ir(III)), like their isoelectronic Ru(II) and Os(II) counter parts $[(arene)M(II)Cl_2]_2$, has been considerable. Frequently ideas and advances made in chemistry relating to the C_5Me_5 systems can be adopted for the arene systems and vice-versa. Thus $[(C_5Me_5)MCl_2]_2$ systems have been used to prepare a vast array of derivative materials containing the $M(III)(C_5Me_5)^{2+}$fragment[176,177]. Facile bridge-cleavage reactions of $[(C_5Me_5)MCl_2]_2$ by a variety of Lewis bases provide a valuable route to mono-metallic derivatives[96,97].

A rapid, room-temperature reaction occurs when (6) and $[(C_5Me_5)MCl_2]_2$ are mixed in a 2:1 molar ratio in chloroform. Treatment of the reaction solution with methanol does not effect precipitation of a solid product and diethyl ether must be used to precipitate the dark red (M=Rh) or orange (M=Ir) products. This has the undesirable result of contaminating the products with amounts of NH_2R_2Cl which would otherwise have been soluble in methanol. It was therefore difficult to obtain scrupulously pure products in these reactions. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the rhodium product run in $CDCl_3$ shows a single 1:4:1 triplet of doublets resonance (δP 27.8 p.p.m., $^1J_{PtP}$ 3570.7Hz, $^2J_{RhP}$ 1.4Hz) consistent with the formation of the six-membered ring $\overline{RhSPPtPS}$. In the high resolution ^1H n.m.r. spectrum an intense singlet is identified at 1.69 p.p.m. which is assigned to the protons of the C_5Me_5 ring. In the $^{13}C-\{^1H\}$ n.m.r. spectrum two signals are evident for this ring at 8.8 and 95.5 p.p.m. with the latter showing a

7.3Hz coupling indicative of $^{1}J_{RhC}$ coupling. Signals for the diethyldithiocarbamate ligand appear in typical positions in the ^{1}H ($\delta_{C\underline{H}_2}$ 3.44q, $\delta_{C\underline{H}_3}$ 1.10t p.p.m.) and $^{13}C-\{^{1}H\}$ ($\delta_{\underline{C}H_2}$ 43.3, $\delta_{\underline{C}H_3}$ 12.2, $\delta_{\underline{C}N}$ 206.2 p.p.m.) n.m.r. spectra with integration of the ^{1}H n.m.r. data confirming the presence of one C_5Me_5 ring for one $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ unit in the product. The nujol mull i.r. spectrum of the red solid shows ν_{CN}=1510 cm^{-1} and ν_{PS}=585 cm^{-1} but as with (71) no M-Cl stretch could be detected. However the product gave no solution conductivity in methylene chloride this, together with microanalytical data suggests the product should be formulated as the neutral heterobimetallic $[(C_5Me_5)RhCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (89), derived from simple bridge cleavage of $[(C_5Me_5)RhCl_2]_2$ by the anionic, platinum-ligand (6, R=Et).

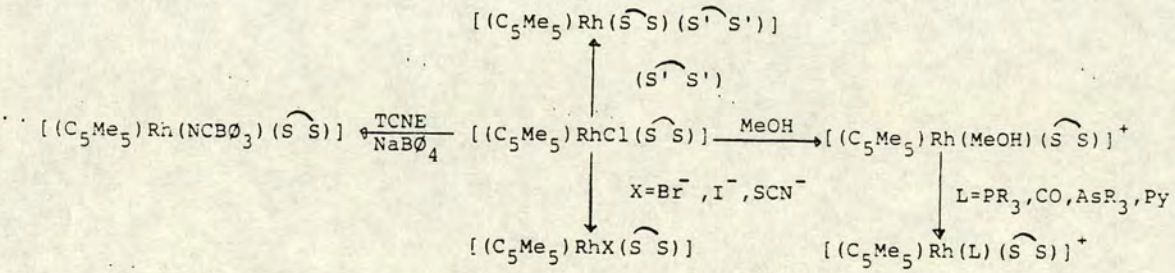


	M	X	R
(89)	Rh	Cl	Et
(90)	Ir	Cl	^{i}Pr
(91)	Rh	I	^{i}Pr

The orange iridium complex $[(C_5Me_5)IrCl(SPPh_2)_2Pt-(S_2CN^{i}Pr_2)]$ (90) was characterised by similar methods. Finally if the iodo-bridged, binuclear complex $[(C_5Me_5)RhI_2]_2$ is treated with two equivalents of (6, ^{i}Pr) in chloroform the dark-purple, iodo complex $[(C_5Me_5)RhI(SPPh_2)_2Pt(S_2CN^{i}Pr_2)]$ (91) can be recovered in reasonable yield.

3.4.2 DERIVATIVES OF THE HETEROBIMETALLICS $[(C_5Me_5)MCl(SPPh_2)_2Pt(S_2CNR_2)]$ (89,90)

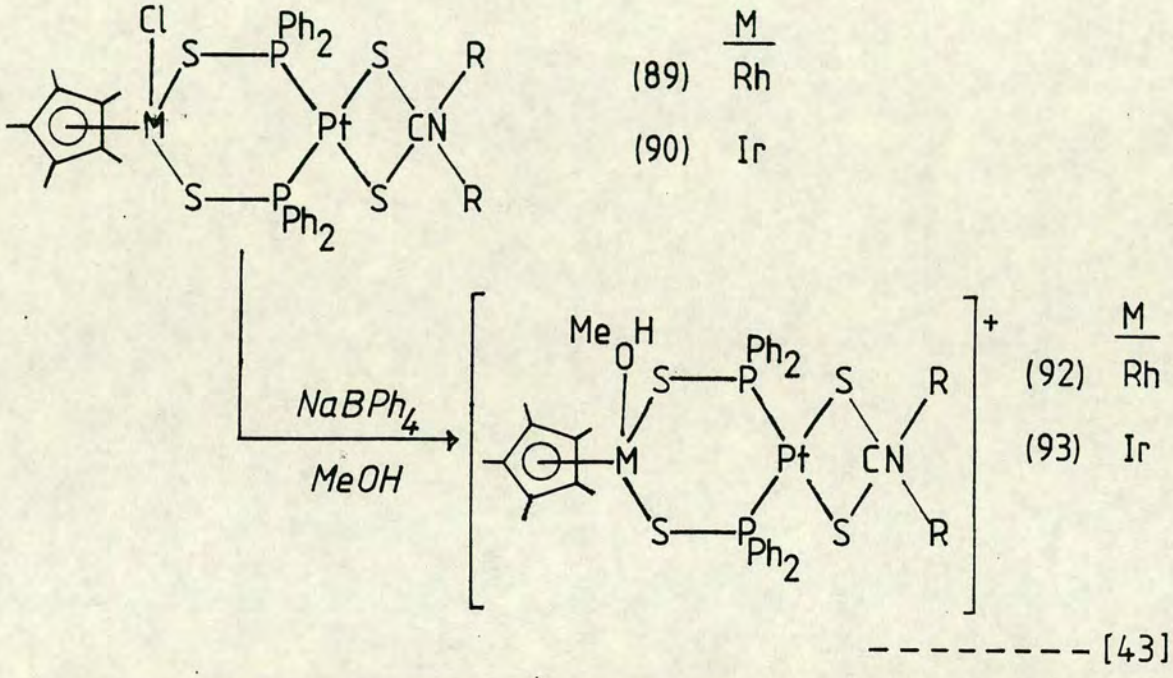
The reaction of $[(arene)RuCl_2]_2$ with various dithioacid ligands is only successful for some dithiophosphinates ($S_2PR_2^-$) [Figure 15, (c) and (d)]. In contrast the reaction of $[(C_5Me_5)MCl_2]_2$ with a wide variety of dithioacid systems ($S\frown S$) is viable producing mononuclear systems of the type $[(C_5Me_5)Rh(S\frown S)Cl]$ ($S\frown S = S_2CNMe_2^-$, $S_2PMe_2^-$, $S_2PPh_2^-$) and $[(C_5Me_5)M(S\frown S)_2]$ (M=Rh, $S\frown S = S_2CNR_2^-$, $S_2PR_2^-$, S_2COR^-; M=Ir, $S\frown S = S_2CNMe_2^-$, $S_2PMe_2^-$). The complex $[(C_5Me_5)Rh(S\frown S)Cl]$ has proved to be a useful precursor for the synthesis of a wide range of neutral and monocationic rhodium(III) species containing the $C_5Me_5^-$ and $(S\frown S)^-$ fragments [Scheme 12][158,167].



Scheme 12: Some chemistry of $[(C_5Me_5)Rh(S\frown S)Cl]$ complexes

The heterobimetallics $[(C_5Me_5)MCl(SPPh_2)_2Pt(S_2CNR_2)]$ (89,90) formed in the 2:1 molar reaction of (6) and $[(C_5Me_5)MCl_2]_2$ (M=Rh, Ir) cannot be isolated by addition of methanol to the reaction solution as for the heterobimetallics (71-76) and Et_2O must be used as the precipitating

solvent. However, if methanolic $NaBPh_4$ is added to the reaction solution a solid is precipitated. All available data supports the formation of the methanol complex $[(C_5Me_5)M(MeOH)(SPPh_2)_2Pt(S_2CNR_2)]BPh_4$ ((92) M=Rh, R=Et; (93) M=Ir, R=^{1}Pr) [Equation 43].

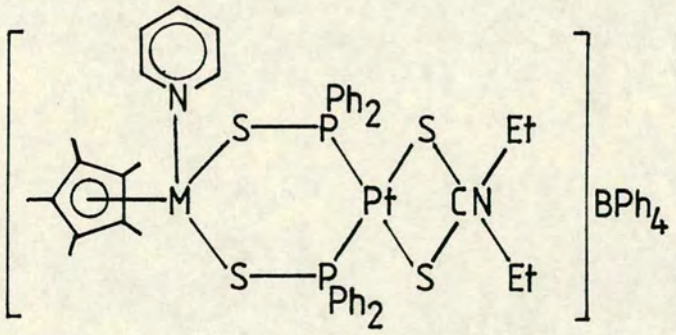


[43]

The use of (92) and (93) as potential synthetic precursors, like $[(C_5Me_5)Rh(MeOH)(S\frown S)]^+$ [Scheme 12], was not fully investigated. However, preliminary evidence suggests that (92), like (89), might be prone to bridge cleavage by Lewis bases with subsequent breakdown of the bimetallic unit.

The pyridine derivatives $[(C_5Me_5)M(py)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ were prepared using method B (Section 3.3.2) by the equimolar reaction of (6, R=Et) and $[(C_5Me_5)MCl_2py]$ in $CDCl_3$. Addition of methanolic $NaBPh_4$ precipitated the brown ((94) M=Rh) and green ((95) M=Ir) products. The

^{1}H n.m.r. spectra for (94) and (95) are very similar and fully consistent with the proposed formulations. The spectrum for (95) shows the ethyl groups of the dithiocarbamate ligand as a quartet ($\delta_{\underline{CH}_2}$ 3.37 p.p.m.) and triplet ($\delta_{\underline{CH}_3}$ 1.08 p.p.m.) resonance and the protons of the C_5Me_5 ring as a singlet at 1.26 p.p.m. A 'doublet' signal appears at 8.54 p.p.m. and is assigned to the pyridine ligand (probably the α-protons to nitrogen). The complex signals in the region 6.8-7.6 p.p.m. for the various phenyl groups also mask the remaining heteroaromatic resonances. The i.r. spectra for (94) and (95) show, in addition to ν_{CN}=1532 cm^{-1}, ν_{PS}=583 cm^{-1} and bands associated with the BPh_4^- ion, a medium-intensity band at 1600 cm^{-1}, which is assigned as a pyridine ligand vibration. Microanalytical results for the products indicate that one $CHCl_3$ molecule of solvation is present for each product molecule in the microcrystalline solids.



M

(94) Rh

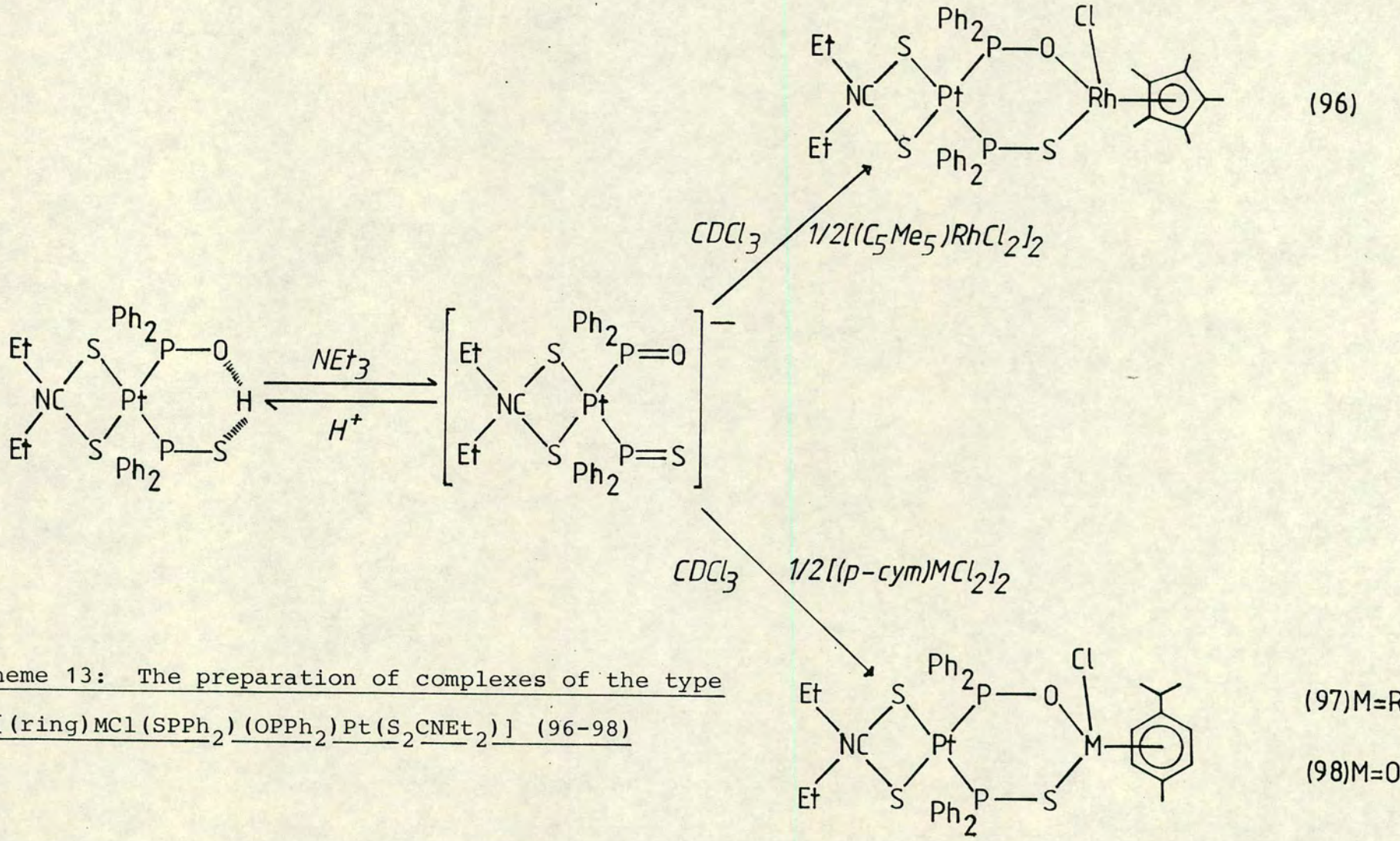
(95) Ir

3.5 REACTION OF $[Pt(S_2CNR_2)(Ph_2PO)(Ph_2PS)H]$ WITH $[(C_5Me_5)RhCl_2]_2$ AND $[(p\text{-cym})MCl_2]_2$ (M=Ru,Os)

Addition of 0.5 molar equivalents of either $[(C_5Me_5)RhCl_2]_2$ or $[(p\text{-cym})MCl_2]_2$ (M=Ru,Os) to a $CDCl_3$ solution containing the $[Pt(S_2CNEt_2)(Ph_2PS)(Ph_2PO)]^-$ anion (formed *in situ* by deprotonation of $[Pt(S_2CNEt_2)(Ph_2PS)(Ph_2PO)H]$ with NEt_3) gives a rapid room temperature reaction to generate the mixed *S,O*-bridged heterobimetallics $[(C_5Me_5)RhCl(OPPh_2)(SPPh_2)Pt(S_2CNEt_2)]$ (96) and $[(p\text{-cym})MCl(OPPh_2)(SPPh_2)Pt(S_2CNEt_2)]$ ((97) M=Ru, (98) M=Os) respectively. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the complexes (96-98) show two resonances (δP_O and δP_S) of 1:4:1 triplet ($^1J_{PtP}$) of doublet ($^2J_{PsPo}$) multiplicity with a further doublet splitting ($^2J_{RhP}$) observed for (96) [Scheme 13]. ^1H n.m.r. and analytical data for the recovered dark-red product (96) and *in situ* ^1H n.m.r. evidence for (98) supports the proposed mixed-bridged formulations.

3.6.1 REACTION OF $[Pt(S_2CNR_2)(Ph_2PO)_2H]$ WITH $[(C_5Me_5)RhCl_2]_2$ AND $[(p\text{-cym})RuCl_2]_2$

$^{31}P\text{-}\{^1H\}$ n.m.r. studies reveal that when 0.5 molar equivalents of either $[(C_5Me_5)RhCl_2]_2$ or $[(p\text{-cym})RuCl_2]_2$ are mixed in a $CDCl_3$ solution containing the 'oxyring-anion' $[Pt(S_2CNEt_2)(Ph_2PO)_2]^-$ (formed *in situ* by deprotonation of (2) with NaOMe [Equation 4]) the *O,O*-bridged heterobimetallic species $[(C_5Me_5)RhCl(OPPh_2)_2Pt(S_2CNEt_2)]$ (99)



Scheme 13: The preparation of complexes of the type [(ring)MCl(SPPh$_2$)(OPPh$_2$)Pt(S$_2$CNEt$_2$)] (96-98)

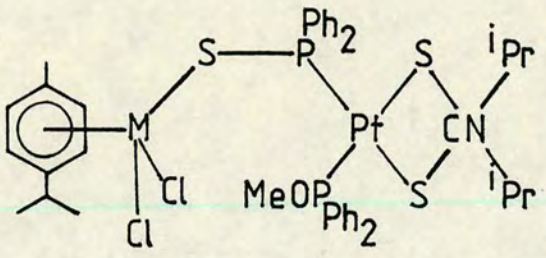
(δP 59.7 p.p.m., $^{1}J_{PtP}$ 3759.9Hz, $^{2}J_{RhP}$ 1.5Hz) and [(p-cym)RuCl(OPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (100) (δP 61.1 p.p.m., $^{1}J_{PtP}$ 3732.9Hz) are formed respectively. Despite several attempts the heterobimetallics (99) and (100) could not be obtained pure and were always isolated contaminated with quantities of [Pt(S$_2$CNEt$_2$)(PH$_2$PO)$_2$H] (2).

3.6.2 REACTION OF [IrHCl(dpae-As,As)(Ph$_2$PO)$_2$H] WITH [(C$_5$Me$_5$)RhCl$_2$]$_2$ AND [(p-cym)RuCl$_2$]$_2$

When [IrHCl(dpae-As,As)(Ph$_2$PO)$_2$H] (3)[8] and [(p-cym)RuCl$_2$]$_2$ are mixed in CDCl$_3$ in a 2:1 molar ratio in the presence of excess NEt$_3$ a slow room-temperature reaction occurs. If monitored *in situ* by ^{31}P-{^{1}H} n.m.r. spectroscopy the single peak for (3) (δP 44.9 p.p.m.) is replaced quantitatively over a 4 hour period by a similar peak at higher frequency (δP 63.0 p.p.m.). The ^{1}H n.m.r. spectrum of the reaction solution reveals a triplet hydride resonance at -21.86 p.p.m. ($^{2}J_{PH}$ 10.8Hz) and also signals for co-ordinated p-cymene. On this information the product is tentatively proposed as the Ir(III)/Ru(II) heterobimetallic [(dpae-As,As)IrHCl(μ-Ph$_2$PO)$_2$RuCl(p-cymene)]. A similar reaction is proposed for (3) and [(C$_5$Me$_5$)RhCl$_2$]$_2$ to give [(dpae-As,As)IrHCl(μ-PPh$_2$O)$_2$RhCl(C$_5$Me$_5$)] with the *in situ* ^{31}P-{^{1}H} n.m.r. spectrum in this case also revealing a doublet coupling in the product resonance (δP 56.2 p.p.m., $^{2}J_{RhP}$ 1.0Hz).

3.7 REACTION OF $[Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2POMe)]$ WITH $[(p\text{-cym})MCl_2]_2$ (M=Ru,Os)

When $[Pt(S_2CN^iPr_2)(Ph_2PS)(Ph_2POMe)]$ (9, R=^{i}Pr) is mixed with $[(p\text{-cym})MCl_2]_2$ (M=Ru,Os) in a 2:1 molar ratio in $CDCl_3$ an immediate reaction occurs to produce the neutral, singly-bridged, heterobimetallic complexes $[Pt(S_2CN^iPr_2)(Ph_2POMe)(\mu\text{-}Ph_2PS)MCl_2(p\text{-cym})]$ ((101) M=Ru; (102) M=Os).



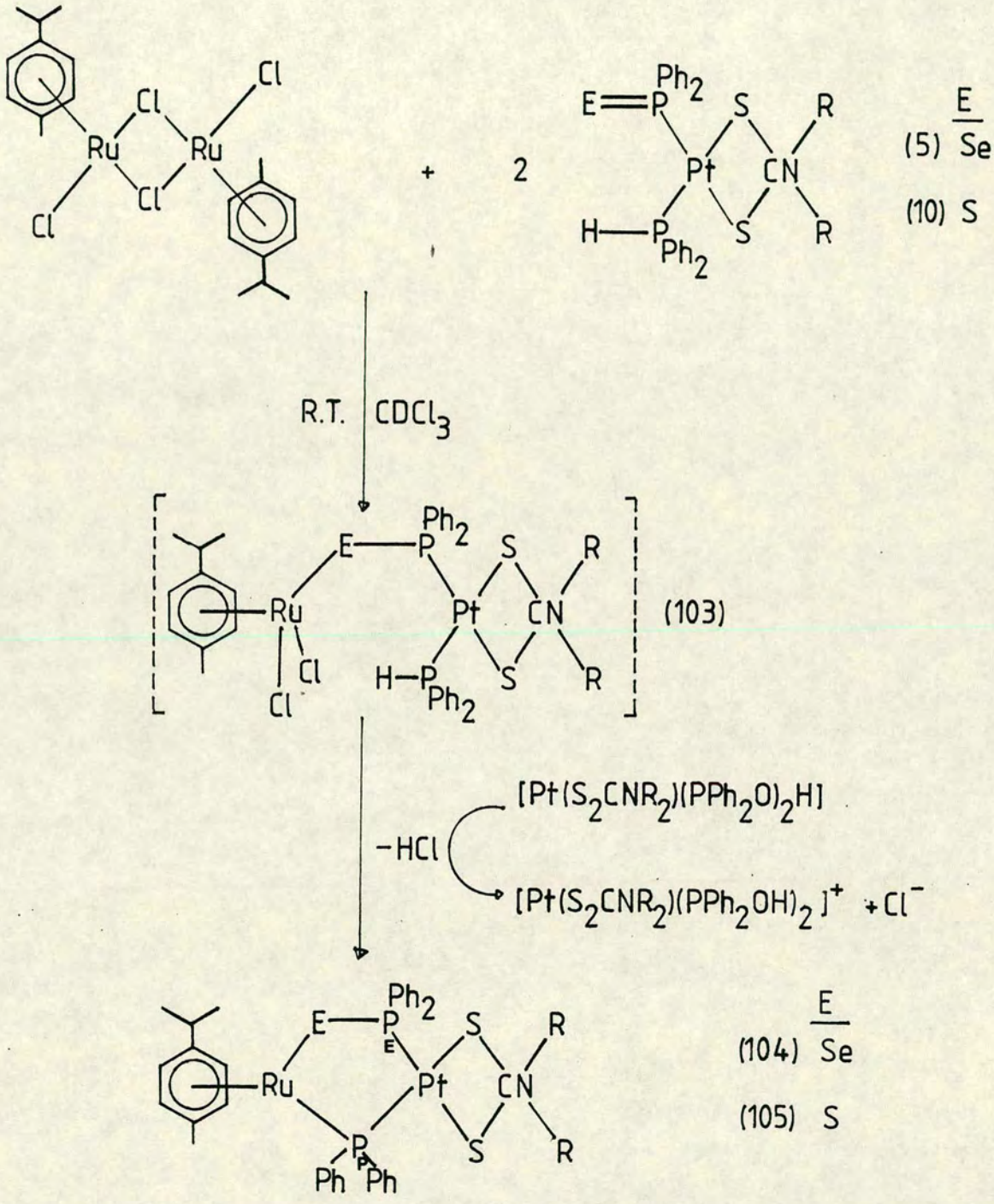
	M
(101)	Ru
(102)	Os

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra for (101) and (102), like (9, R=^{i}Pr), consist of two sets of 1:4:1 triplet of doublet resonances. A comparison of the n.m.r. data for (9, R=^{i}Pr) and the products (101-102) reveals a considerable shift in the position of the thiophosphorus resonance (δP 28.2 for (9, ^{i}Pr), 72.3 for (101) and 87.0 p.p.m. for (102)), while the position of the methoxyphosphorus resonance is altered only slightly (δP 92.7 for (9, ^{i}Pr), 93.0 for (101) and 95.7 p.p.m. for (102)). This evidence suggests that during the reaction the basic $[Pt(S_2CN^iPr_2)(Ph_2POMe)(Ph_2PS)]$ unit remains intact, with the observed shift in the thiophosphorus resonance due to coordination of a metal fragment at sulphur. The i.r. spectrum for the isolated product

(101) shows ν_{PS} at 575 cm^{-1}, which compares with the ν_{PS} stretching frequency found for (9, R=^{i}Pr) of 605 cm^{-1} and is consistent with a reduction in P-S bond order on forming the phosphine-sulphide bridge. No solution conductivity was found for (101) in CH_2Cl_2.

3.8 REACTION OF $[Pt(S_2CNR_2)(Ph_2P_EE)(Ph_2P_PH)]$ WITH $[(p\text{-cym})RuCl_2]_2$ AND $[(C_5Me_5)RhCl_2]_2$ [183]

Reaction of $[Pt(S_2CNEt_2)(Ph_2P_SS)(Ph_2P_PH)]$ (10, R=Et) and $[(p\text{-cym})RuCl_2]_2$ in a 2:1 molar ratio in $CDCl_3$ proceeds to give the phosphido-/phosphine chalcogenide-bridged heterobimetallic $[(p\text{-cym})RuCl(\mu\text{-}SP_SPh_2)(\mu\text{-}P_PPh_2)Pt(S_2CNEt_2)]$ (105). The formation of (105) (and 104) is presumably *via* the elimination of HCl from the undetected intermediate (103) [Scheme 14].



Scheme 14: Formation of [(p-cym)RuCl(EPPh$_2$)(PPh$_2$)Pt-(S$_2$CNEt$_2$)] (E=S (105), Se (104))

Indirect evidence for the proton loss from the secondary-phosphine moiety in (103) is provided by performing the reaction in the presence of 10 mg of $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ (2). The $^{31}P-\{^1H\}$ n.m.r. spectrum of the reaction solution, in addition to the signals for (105), reveals a shift in δP for (2) from 61 to 71.0 p.p.m. which from earlier work is consistent with the formation of $[Pt(S_2CNEt)(Ph_2POH)_2]^+$. Deprotonation of (10) is not observed on direct treatment with (2) and, since formation of the dibridged product is achieved in the absence of a base, it is clear that protonation of (2) occurs after elimination of HCl from (103). The $^{31}P-\{^1H\}$ n.m.r. spectrum for (105) consists of two sets of 1:4:1 triplet of doublet resonances with no further splitting observed on retention of proton coupling. A comparison of the $^{31}P-\{^1H\}$ n.m.r. spectrum of the selenium analogue of (105) $[(p\text{-cym})RuCl(SeP_{Se}Ph_2)(P_PPh_2)Pt(S_2CNEt_2)]$ (104) [Figure 19], prepared by reaction of (5) with $[(p\text{-cym})RuCl_2]_2$, enables the higher-frequency resonance in both spectra to be assigned as δP_E ((104) δP_{Se} 52.5 p.p.m., $^1J_{SeP}$ 399.0Hz, ^{77}Se, $I=\frac{1}{2}$, 7.6% abundant; (105) δP_S 74.7 p.p.m. c.f. δP_S 72.3 p.p.m. for (101)) with the phosphido resonance δP_P ((104) δP_P 28.5, (105) δP 26.1 p.p.m.) appearing in the region generally considered as typical for these bridging ligands where no metal-metal bond exists[184-186]. The assignment of the phosphorus signals for the isoelectronic Rh analogue of (104), $[(C_5Me_5)RhCl(SeP_{Se}Ph_2)(P_PPh_2)Pt(S_2CNEt_2)]$ (106), prepared by reaction of (5) with $[(C_5Me_5)RhCl_2]_2$, is further

enhanced with the appearance of $^{1}J_{RhP}$ coupling on δP_P (δP_P 17.5 p.p.m., $^{1}J_{RhP}$ 125.4Hz) and $^{1}J_{SeP}$ on δP_{Se} (δP_{Se} 40.5 p.p.m. $^{1}J_{SeP}$ 371.3Hz). The cis-coupling constant $^{2}J_{P_EP_P}$ is reduced from 24Hz in the starting compounds to 5.9Hz (104), 10.9Hz (105) and 6.7Hz (106) in the products, which suggests that formation of the five-membered, dimetallic-ring system is accompanied by changes in important bond angles such as $P_E\hat{P}tP_P$. No comparable change in cis-coupling constant is measured on formation of the complexes (96-98) which contain a less sterically demanding six-membered, dimetallic-ring system. The ^{1}H and ^{13}C n.m.r. spectra for (104) reveal an unusually complicated set of signals for the p-cymene ring and suggest that considerable steric hindrance to free rotation exists for this group in the molecule at room temperature. No similar effect is observed for the C_5Me_5 ring in complex (106). The red complexes (104) and (106) can be isolated in high yield on addition of diethyl ether to the reaction solutions. The molecular weight of (104) was determined osmetrically in acetone against a benzyl standard as 1030 (calculated 1062) and microanalytical data, including %P and %S results, support the proposed formulation. The i.r. spectrum shows bands for ν_{CN}=1516, ν_{PSe}=530 and ν_{RuCl}=290 cm^{-1} and both (104) and (106) are non-conducting in CH_2Cl_2 solution. Complex (105) was not isolated and no attempt was made to characterise the proposed intermediate (103) by working at low temperature.

3.9 REACTION OF $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ WITH $[(p\text{-cym})MCl_2]_2$ (M=Ru,Os)

A yellow solid can be recovered in low yield from the green-brown solution produced on refluxing $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (8) and $[(p\text{-cym})OsCl_2]_2$ in a 2:1 molar ratio in chlofororm for 4½ hours. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the product reveals two related P resonances at 69.0 and 85.6 p.p.m. each comprising of a 1:4:1 triplet of 1:4:1 triplet of doublets splitting revealing $^2J_{PP}$, $^1J_{PtP}$ and $^2J_{PtP}$ couplings. The poorly resolved ^1H n.m.r. spectrum suggests that one 'Os(p-cymene)' moiety is present for each unit of (8) in the product. The KBr disc i.r. spectrum of the product shows a down-frequency shift in the band associated with ν_{PS} from 583 in (8) to 550 cm^{-1} and an up-frequency shift in ν_{CN} of 20 cm^{-1} to 1538 cm^{-1}. A similar reaction occurs when (8) and $[(p\text{-cym})RuCl_2]_2$ are refluxed in chloroform but in this case two diplatinum products have been observed by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. The products show slight conductivity in methanol solution. Microanalytical data on Cl^- and PF_6^- isolated products does not distinguish between the formulations $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2MCl(p\text{-cym})\}X$ and $\{[Pt(S_2CNEt_2)(Ph_2PS)]_2M_2Cl_2(p\text{-cym})_2\}2X$.

Additional effort is required to determine fully the nature of these species. It is likely that the major-product produced has a single $MCl(p\text{-cym})^+$ fragment bound by the bridging-sulphur atoms (see bonding mode of (8) in

compounds (67) and (68)). However, either the coordination of a MCl_2(p-cymene) fragment by one of the bridging-sulphur atoms or metal coordination involving the dithiocarbamate ligand sulphur atoms cannot be discounted.

3.10 CONCLUSIONS

The platinum complexes (2) and (5-10), containing phosphine chalcogenide ligands, bridge-cleave the dichloro-bridged systems $[(arene)MCl_2]_2$ (M=Ru,Os) and $[(C_5Me_5)MCl_2]_2$ (M=Rh,Ir) to form symmetric, asymmetric and mixed bridged, heterobimetallic complexes. A limited investigation of the chemistry of the heterobimetallic complexes $[(arene)MCl(\mu\text{-}SPPh_2)_2Pt(S_2CNR_2)]$ (M=Ru,Os) has shown that the terminal chloride ligand can be substituted by ligands such as PR_3, CO and diphosphines. There is every possibility that a similar coordination chemistry could be developed for the asymmetric and mixed bridged heterobimetallic systems.

3.11 EXPERIMENTAL

3.11.1 MATERIALS

Platinum metals were obtained from Johnson Matthey PLC. $[(arene)RuCl_2]_2$ (arene=C_6H_6, p-cymene [141], C_6Me_6 [181]), $[(p\text{-cymene})OsCl_2]_2$ [142], $[(C_5Me_5)RhCl_2]_2$, $[(C_5Me_5)IrCl_2]_2$ [96,97], derivatives thereof and all platinum complexes[26] were prepared by standard literature methods.

3.11.2 PREPARATION OF HETEROBIMETALLICS $[(arene)MCl(\mu\text{-}SPPh_2)_2Pt(S_2CNR_2)]$ (71-76) $[(C_6H_6)RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (71). $[(C_6H_6)RuCl_2]_2$ (66 mg, 0.13 mmole) was stirred in chloroform (10 ml) for 15 minutes. $[NH_2Et_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (224 mg, 0.26 mmole) was added in three portions (75 mg) and stirring continued for a further 15 minutes. The reaction solution was reduced in volume and addition of methanol (15 ml) precipitated the red product which was collected by filtration, washed with MeOH and Et_2O and finally dried *in vacuo* at 56°C for 3 hours. Yield 200 mg, 77%; m.p. 215°C decomposition; Found: C, 42.26; H, 3.68; N, 1.43; Calc. for $C_{35}H_{36}NS_4P_2ClRuPt$, C, 42.36; H, 3.66; N, 1.41; KBr disc i.r. spectrum ν_{CN} 1525, ν_{PS} 584 cm^{-1}. The heterobimetallics (72-76) were prepared similarly from the appropriate combination of starting materials $[(arene)MCl_2]_2$ and (6). $[(p\text{-cym})RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (72) Yield 80%; m.p. 185°C; Found: C, 44.59; H, 4.24; N, 1.31; S, 11.96; P, 6.22; m.wt. 968 (osmometry); Calc. for $C_{39}H_{44}NS_4P_2ClRuPt$, C, 44.67; H, 4.23; N, 1.34; S, 12.23; P, 5.91;

m.wt. 1004. Mull i.r. spec. ν_{CN} 1510, ν_{PS} 589 cm^{-1}. [(p-cym)RuCl(SPPh$_2$)$_2$Pt(S$_2$CN^{i}Pr$_2$)] (74) Yield 75%; m.p. 210°C d. Found: C, 45.10; H, 4.41; N, 1.63; Calc. for $C_{41}H_{48}NS_4P_2ClRuPt$, C, 45.78; H, 4.50; N, 1.30. [(C$_6$Me$_6$)RuCl(SPPh$_2$)$_2$Pt(S$_2$CN^{i}Pr$_2$)] (75) Yield 65%; m.p. >230°C. Found: C, 46.68; H, 4.78; N, 1.18. Calc. for $C_{43}H_{58}NS_4P_2ClRuPt$, C, 46.50; H, 5.26; N, 1.26. KBr disc i.r. spectrum ν_{CN} 1495, ν_{PS} 585 cm^{-1}. [(p-cym)OsCl-(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (76) Yield 70%; m.p. 225°C.d. Found: C, 41.03; H, 3.82; N, 1.03; Calc. for $C_{39}H_{44}NS_4P_2ClOsPt$, C, 41.17; H, 3.90; N, 1.23. Mull i.r. spectrum ν_{CN} 1515, ν_{PS} 590, ν_{OsCl} 282 cm^{-1}.

3.11.3 PREPARATION OF DERIVATIVES OF THE HETEROBIMETALLICS (71-76) [(C$_6$H$_6$)(PPh$_2$Et)Ru(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)]BPh$_4$ (77). METHOD A. [(C$_6$H$_6$)RuCl(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (71) (43 mg, 0.04 mmole) and PPh$_2$Et (2 drops, ∿15 mg) were refluxed in chloroform (10 ml) under dinitrogen for 2 hours. The red solution was reduced in volume and methanolic NaBPh$_4$ added to precipitate the light-brown product, which was collected, washed with MeOH and dried *in vacuo* at 56°C for 4 hours. Yield 65%, Found: C, 58.63; H, 4.65; N, 0.94; Calc. for $C_{73}H_{71}NS_4P_3BRuPt$, C, 58.84; H, 4.77; N, 0.94. KBr disc i.r. spectrum ν_{CN} 1525, $\nu_{BPh_4^-}$ 700, ν_{PS} 584 cm^{-1}. Similarly prepared was [(p-cym)PPh$_2$EtRu(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)]-BPh$_4$ (78) from (72) and PPh$_2$Et. Yield 60%, Found: C, 59.68; H, 5.00; N, 0.86; Calc. for $C_{77}H_{79}NS_4P_3BRuPt$; C, 59.87; H, 5.51; N, 0.91. KBr disc i.r. spectrum

ν_{CN} 1528, $\nu_{BPh_4^-}$ 700, ν_{PS} 584 cm^{-1}. [(p-cym)PPh_3Ru-($SPPh_2$)$_2$Pt(S_2CNEt_2)]BPh_4 (79) METHOD B. [(p-cym)$RuCl_2$-PPh_3] (100 mg, 0.18 mmole) and [NH_2Et_2][Pt(S_2CNEt_2)-(Ph_2PS)$_2$] (150 mg, 0.18 mmole) were refluxed in chloroform (10 ml) under dinitrogen for 4 hours. Methanolic $NaBPh_4$ was then added to precipitate the brown product. Yield 35%. Characterisation based on $^{31}P-\{^1H\}$ n.m.r. evidence. [(p-cym)RuCO($SPPh_2$)$_2$Pt(S_2CNEt_2)]BPh_4 (80) Method B. Prepared by the rapid equimolar reaction of [(p-cym)$RuCl_2$CO] and (6, R=Et) in $CDCl_3$, and isolated in an impure form as a brown solid on addition of methanolic $NaBPh_4$ to the reaction solution. Mull i.r. spectrum ν_{CO} 2015, ν_{CN} 1524, ν_{PS} 588 cm^{-1}. [(p-cym)OsCO($SPPh_2$)$_2$Pt(S_2CNEt_2)]BPh_4 (81) Method A. CO was bubbled through a $CDCl_3$ solution containing [(p-cym)OsCl-($SPPh_2$)$_2$Pt(S_2CNEt_2)] (76) for 4 minutes. Addition of methanolic $NaBPh_4$ to the reaction solution precipitated a yellow solid which was collected by filtration, washed with MeOH and dried *in vacuo* at 56°C for 2 hours. Yield 60%. Found: C, 50.7; H, 3.8; N, 0.9; Calc. for $C_{64}H_{64}NS_4P_2OBOsPt$, C, 53.0; H, 4.4; N, 1.0 (contaminated with MeOH). KBr disc i.r. spectrum ν_{CO} 1995, ν_{CN} 1528, ν_{PS} 586 cm^{-1}. [(p-cym)Os(PhCCH)($SPPh_2$)$_2$Pt(S_2CNEt_2)]BPh_4 (82) Method A. Prepared by mixing (76) and a slight molar excess of PhCCH in $CDCl_3$ with isolation of the impure product on addition of methanolic $NaBPh_4$ to the reaction solution. KBr disc i.r. spectrum $\nu_{C\equiv C}$ 2000, ν_{CN} 1518, ν_{PS} 578 cm^{-1}. [(p-cym)Ru($Ph_2P(CH_2)_2CH.CH_2$)($SPPh_2$)$_2$Pt(S_2CNEt_2)]BPh_4 (83) Method A. Prepared by mixing (72) with a slight molar excess

of $Ph_2P(CH_2)_2CH=CH_2$ in $CDCl_3$. The pink solid recovered on addition of methanolic $NaBPh_4$ to the reaction solution decomposed on standing in air. [(p-cym)Ru(dppm-P)$(SPPh_2)_2$-Pt(S_2CNEt_2)] (84). Prepared by mixing an equimolar quantity of [(p-cym)RuCl$(SPPh_2)_2$Pt(S_2CNEt_2)] (72) and dppm in $CDCl_3$ at room temperature with addition of methanolic $NaBPh_4$ giving a red solid which was collected, washed with MeOH and dried *in vacuo* at 56°C for 3 hours. Yield 71%, m.p. 154°C.d. Found: C, 60.73; H, 5.07; N, 1.13; Calc. for $C_{88}H_{86}NS_4P_4$ BRuPt C, 61.57; H, 5.05; N, 0.82. [(p-cym)Ru(dppe-P)-$(SPPh_2)_2$Pt(S_2CNEt_2)]BPh_4 (85). Prepared as for (84) using (72) and dppe. Yield 75%. [(Et_2NCS_2)Pt(μ-$Ph_2PS)_2$Ru-(p-cym)(μ-dppe)Os(p-cym)(μ-$SPPh_2)_2$Pt(S_2CNEt_2)][BPh_4]$_2$ (86). The complex [(p-cym)Ru(dppe-P)$(SPPh_2)_2$Pt(S_2CNEt_2)]Cl was formed *in situ* by mixing (72) (53 mg, 0.05 mmole) and dppe (20 mg, 0.05 mmole) in $CDCl_3$ (2 ml). [(p-cym)OsCl$(SPPh_2)_2$-Pt(S_2CNEt_2)] (76) (58 mg, 0.05 mmole) was added to immediately form the titled product which was precipitated on addition of methanolic $NaBPh_4$ washed with portions of MeOH and dried *in vacuo* for 2 hours. Yield 120 mg, 75% m.p. 100°C.d. Found: C, 56.9; H, 4.8; N, 0.9; calc. for $C_{152}H_{152}N_2S_8P_6B_2RuOsPt_2$ C, 57.9; H, 4.9; N, 0.9. KBr disc i.r. spectrum ν_{CN} 1522, $\nu_{BPh_4^-}$ 700, ν_{PS} 580 cm^{-1}. $^{31}P-\{^1H\}$ n.m.r. spectrum in $CDCl_3$ at 298°K. See Section 3.3.7. ^1H n.m.r. spectrum in $CDCl_3$ at 298°K. p-cymene rings: $\delta_{C\underline{H}_3}$ 1.53, 1.65 p.p.m. singlets, $\delta_{CH(C\underline{H}_3)_2}$ 0.45 p.p.m. overlapping doublets, $\delta_{C_6\underline{H}_4}$ broad humps 5-6 p.p.m.;

$\delta_{CH_2\underline{C}H_3}$ 1.15 p.p.m. overlapping triplets, $\delta_{\underline{C}H_2CH_3}$ 3.43 p.p.m. overlapping quartets; Phenyl groups 6.8-7.5 p.p.m.; Slope of Λ_o-Λ_e against $Ce^{\frac{1}{2}}$ plot in CH_2Cl_2 590.

3.11.4 PREPARATION OF HETEROBIMETALLICS [$(C_5Me_5)MX(\mu\text{-}SPPh_2)_2Pt(S_2CNR_2)$] (89-91), [$(C_5Me_5)RhCl(SPPh_2)_2Pt(S_2CNEt_2)$] (89). $[(C_5Me_5)RhCl_2]_2$ (50 mg, 0.081 mmole) was stirred with $[NH_2Et_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ (140 mg, 0.16 mmole) in chloroform (8 ml) for 5 minutes. Et_2O (30 ml) was added to precipitate the dark-red product, which was collected, washed with a small quantity of ice-cold methanol and dried *in vacuo*. Yield 125 mg, 72%, m.p. 214°C. Found: C, 44.39; H, 4.13; N, 1.31; Calc. for $C_{39}H_{45}NS_4P_2ClRhPt$, C, 44.55; H, 4.31; N, 1.33. Mull i.r. spectrum ν_{CN} 1510, ν_{PS} 585 cm^{-1}. [$(C_5Me_5)IrCl(SPPh_2)_2Pt(S_2CN^iPr_2)$] (90). Prepared as for (89) using $[(C_5Me_5)IrCl_2]_2$ and (6, R=^{i}Pr). Yield 65%, m.p. 227°C. Found: C, 42.20; H, 4.26; N, 1.44; Calc. for $C_{41}H_{49}NS_4P_2ClIrPt$, C, 42.14; H, 4.23; N, 1.20. [$(C_5Me_5)RhI(SPPh_2)_2Pt(S_2CN^iPr_2)$] (91). Prepared as for (89) using $[(C_5Me_5)RhI_2]_2$ and (6, R=^{i}Pr). Yield 60%. m.p. >230°C. Found: C, 41.6; H, 4.4; H, 1.1; Calc. for $C_{39}H_{45}NS_4P_2IRhPt$ C, 42.1; H, 4.2; N, 1.2.

3.11.5 PREPARATION OF DERIVATIVES OF THE HETEROBIMETALLICS (89-91). [$(C_5Me_5)Ir(MeOH)(SPPh_2)_2Pt(S_2CN^iPr_2)$]$BPh_4$ (93). (91) in a small volume of chloroform was treated with excess methanol. The colour of the solution changed from orange to green and addition of $NaBPh_4$ allowed the recovery of the

green product. Yield 100%. Found: C, 52.3; H, 4.8; N, 1.2; Calc. for $C_{66}H_{73}NS_4P_2OBIrPt$ C, 53.4; H, 5.0; N, 1.0. Similarly prepared using (89) and MeOH was [$(C_5Me_5)Rh(MeOH)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (92). Yield 100%. KBr disc i.r. spectrum ν_{CN} 1526, ν_{PS} 580, $\nu_{BPh_4^-}$ 700 cm^{-1}; ^1H n.m.r. spectrum in $CDCl_3$ at 298°K $\delta_{C_5Me_5}$ 1.22s (15), $\delta_{CH_2CH_3}$ 1.09t (6), 3.39q (4), δ_{MeOH} 1.54br (3), $\delta_{C_6H_5}$ 6.8-7.7 p.p.m. [$(C_5Me_5)Rh(pyridine)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (94). [$(C_5Me_5)RhCl_2(pyridine)$] (26 mg, 0.067 mmole) and (6, R=Et) (57 mg, 0.067 mmole) were stirred in chloroform (8 ml) for 5 minutes. Addition of methanolic $NaBPh_4$ precipitated the brown product which was collected, washed with methanol and Et_2O and dried *in vacuo*. Yield 80 mg, 85%, m.p. 129°C. Found: C, 54.8; H, 4.7; N, 1.7; Calc. for $C_{69}H_{71}N_2S_4P_2BRhPtCl_3$ (includes $CHCl_3$) C, 54.1; H, 4.7; N, 1.8. KBr disc i.r. spectrum ν_{CN} 1532, ν_{PS} 583, ν_{py} 1600 cm^{-1}. Similarly prepared from [$(C_5Me_5)IrCl_2$-(pyridine)] and (6, R=Et) was [$(C_5Me_5)Ir(pyridine)(SPPh_2)_2$-$Pt(S_2CNEt_2)]BPh_4$ (95). Yield 96%. m.p. 160°C. Found: C, 51.1; H, 4.4; N, 1.7; Calc. for $C_{69}H_{71}N_2S_4P_2BRhPtCl_3$ (includes. $CHCl_3$) C, 51.9; H, 4.4; N, 1.7. KBr disc i.r. spectrum ν_{CN} 1532, ν_{PS} 583, ν_{py} 1600 cm^{-1}.

3.11.6 PREPARATION OF ASYMMETRIC BRIDGED HETEROBIMETALLICS

[$(C_5Me_5)RhCl(\mu\text{-}OPPh_2)(\mu\text{-}SPPh_2)Pt(S_2CNEt_2)]$ (96). The compound [$Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)H$] (126 mg, 0.16 mmole) in $CHCl_3$ (10 ml) was treated with triethylamine (1 ml) to give [$Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)$]$NHEt_3$ *in situ*.

$[(C_5Me_5)RhCl_2]_2$ (51 mg, 0.82 mmole) was added and the reaction solution stirred for 10 minutes under N_2. The solution was filtered and the filtrate reduced to a small volume to precipitate the dark-red product, which was collected, washed with a small amount of MeOH, Et_2O and pentane and dried in vacuo. The product is only partially soluble in $CHCl_3$ but soluble in CH_2Cl_2. Yield 60 mg, 70%. Found: C, 46.7; H, 4.8; N, 1.2; Calc. for $C_{39}H_{45}NS_3OP_2$-ClRhPt, C, 45.3; H, 4.4; N, 1.4. ^1H n.m.r. spectrum in CD_2Cl_2 at 298°K, $\delta_{C_5Me_5}$ 1.64s (15), $\delta_{CH_2CH_3}$ 1.16t two (6), 3.53 two q(4); $\delta_{C_6H_5}$ 7-8 p.p.m. (20); $^{31}P-\{^1H\}$ n.m.r. spectrum in CH_2Cl_2 with d^6-acetone lock at 298°K. (see Table 9).

The complexes [(p-cym)MCl(OPPh$_2$)(SPPh$_2$)Pt(S$_2$CNEt$_2$)] ((97) M=Ru, (98) M=Os) were prepared using $[(p\text{-cym})MCl_2]_2$ and $NHEt_3[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)]$ and characterised in situ by $^{31}P-\{^1H\}$ n.m.r. spectroscopy (see Table 9).

[(p-cym)RuCl(μ-SePPh$_2$)(μ-PPh$_2$)Pt(S$_2$CNEt$_2$)] (104). $[(p\text{-cym})RuCl_2]_2$ (70 mg, 0.11 mmole) and $[Pt(S_2CNEt_2)(Ph_2PSe)$-$(Ph_2PH)]$ (217 mg, 0.22 mmole) were stirred in chloroform (10 ml) for 10 minutes. The solution was reduced in volume and Et_2O added to precipitate the red product which was collected and dried in vacuo. Yield 190 mg, 81%, m.p. 192°C.d. Found: C, 43.94; H, 4.09; N, 1.31; P, 5.64; S, 6.02; m.wt. 1028 (osmometry in acetone),(M+H)-Cl 1028 m/e FAB mass spec. Calc. for $C_{39}H_{44}NS_2SeP_2ClRuPt$ C, 44.04; H, 4.14; N, 1.31, P, 5.83; S, 6.02, m.wt. 1062. KBr disc i.r. spectrum, ν_{CN} 1510, ν_{PSe} 525, ν_{RuCl} 290 cm^{-1}. ^1H n.m.r.

spectrum run in $CDCl_3$ at 298°K. p-cymene ring: $\delta_{C\underline{H}_3}$ 1.67s (3), $\delta_{C\underline{H}Me_2}$ 2.36sep (1), $\delta_{CH(C\underline{H}_3)_2}$ 0.87d (3), 1.03d (3), $\delta_{C_6\underline{H}_4}$ complicated multiplets 4.96-5.5(4); $\delta_{CH_2C\underline{H}_3}$ 1.1t (3), 1.07t (3), $\delta_{C\underline{H}_2CH_3}$ multiplet 3.35-2.50(4); δ_{Phenyl} broad complicated multiplets 7.01-7.90 p.p.m. (20). $^{13}C-\{^1H\}$ n.m.r. spectrum run in $CDCl_3$ at 298°K. p-cymene ring: δ_C 107.8(A), 92.5(B), 88.6 and 88.4(C), 85.5 and 83.3(D), 30.2(E), 22.3 and 21.8(F), 17.2(G). NOTE: Doublet coupling $^2J_{CP} \sim 4.4$Hz visible on (C) and (D) carbon resonances (refer to key Table 11); $\delta_{\underline{C}H_2CH_3}$ 43.8 and 43.6, $\delta_{\underline{C}H_2CH_3}$ 12.2, $\delta_{\underline{C}N}$ 207.4; $\delta_{\underline{C}_6H_5}$ 126.6-141.7 p.p.m. [$(C_5Me_5)RhCl(\mu\text{-}SePPh_2)(\mu\text{-}PPh_2)Pt(S_2CN^iPr_2)$] (106). Prepared as for (104) from $[(C_5Me_5)RhCl_2]_2$ and $[Pt(S_2CN^iPr_2)(Ph_2PSe)(Ph_2PH)]$ Yield 75% KBr disc i.r. spectrum, ν_{CN} 1490, ν_{PSe} 525 cm^{-1}. ^1H n.m.r. spectrum run in $CDCl_3$ at 303°K. $\delta_{C_5\underline{Me}_5}$ 1.35d, $^3J_{PH}$ 3.0Hz; $\delta_{C\underline{H}Me_2}$ 4.3 broad hump, $\delta_{CH(C\underline{H}_3)_2}$ overlapping doublets 1.21; $\delta_{C_6\underline{H}_5}$ 7.0-7.9 p.p.m. $^{13}C-\{^1H\}$ n.m.r. run in $CDCl_3$ at 298°K. $\delta_{C_5Me_5}$ 96.9. $^1J_{RhC}$ 4.4Hz, 9.1; $\delta_{\underline{C}HMe_2}$ 50.7, 50.5, $\delta_{CH(\underline{C}H_3)_2}$ 19.84, 19.75; $\delta_{C_6H_5}$ 126.3-135.7 p.p.m.

REACTION OF $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ WITH $[(p\text{-}cym)MCl_2]_2$ (M=Ru,Os). $[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (73 mg, 0.065 mmole) and $[(p\text{-}cym)OsCl_2]_2$ (27 mg, 0.034 mmole) were refluxed in chloroform (10 ml) for 4½ hours. The green-brown solution obtained was reduced in volume and methanol added to precipitate any unreacted Pt starting material which was removed by filtration. The filtrate was again reduced in volume and diethyl ether added to precipitate the yellow product. Yield 20 mg.

Found: C, 33.9; H, 3.4; N, 1.7; Calc. for $C_{44}H_{54}N_2S_6P_2Cl_2Pt_2OS$, C, 34.9; H, 3.5; N, 1.8. $^{31}P-\{^1H\}$ n.m.r. spectrum run in $CDCl_3$ at 298°K. δP_1 69.0, $^1J_{PtP_1}$ 3887.1, $^2J_{PtP_1}$ 44.9; δP_2 85.6 p.p.m., $^1J_{PtP_2}$ 3932.7Hz, $^2J_{PtP_2}$ 47.1Hz, $^2J_{P_1P_2}$ 11.7Hz. KBr disc i.r. spectrum ν_{CN} 1538, ν_{PS} 550, 573sh cm^{-1}. [Pt(S_2CNEt$_2$)(Ph_2PS)]$_2$ and [(p-cym)$RuCl_2$]$_2$ refluxed in chloroform for two hours to yield on work-up of the reaction solution a brown solid. $^{31}P-\{^1H\}$ n.m.r. spectrum run in $CDCl_3$ at 298°K. Major species: δP_1 59.0, $^1J_{PtP_1}$ 3874.0, $^2J_{PtP_2}$ 49.2; δP_2 77.2 p.p.m., $^1J_{PtP_2}$ 3900.1Hz, $^2J_{PtP_2}$ 50.1Hz, $^2J_{P_1P_2}$ 10.8Hz. Minor species δP_1 59.4, $^1J_{PtP_1}$ ~3910; δP_2 67.7 p.p.m. $^1J_{PtP_2}$ ~4290Hz, $^2J_{PtP_2}$ 48.5Hz, $^2J_{P_1P_2}$ 11.5Hz.

Table 9 Phosphorus-31-{^{1}H} n.m.r. Data for Complexes Discussed in Chapter 3 and Run in $CDCl_3$ at 298°K

	δP_E	$^1J_{PtP_E}$	$^2J_{RhP}$
$[(C_6H_6)RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (71)	37.8	3461.9	
[(p-cym)$RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (72)	33.8	3452.2	
$[(C_6H_6)RuCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (73)[a]	38.3	3394.5	
[(p-cym)$RuCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (74)	34.9	3396.0	
$[(C_6Me_6)RuCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (75)	24.9	3547.4	
[(p-cym)$OsCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (76)	28.4	3464.3	
[(p-cym)$RuCO(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (80)	29.9	3386.2	
[(p-cym)$OsCO(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (81)	26.9	3371.6	
[(p-cym)$Os(HCCPh)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (82)	26.8	3374.0	
[(p-cym)Ru(dpae-As)$(SPPh_2)_2Pt(S_2CNEt_2)]Cl$[a]	42.6	3378.9	
$[(C_5Me_5)RhCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (89)	27.8	3570.7	1.4
$[(C_5Me_5)IrCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (90)	22.7	3433.8	
$[(C_5Me_5)RhI(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (91)	29.6	3503.4	1.1
$[(C_5Me_5)Rh(MeOH)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (92)	28.4	3352.0	n/m
$[(C_5Me_5)Ir(MeOH)(SPPh_2)_2Pt(S_2CN^iPr_2)]BPh_4$ (93)	25.2	3317.9	
$[(C_5Me_5)Rh(pyridine)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (94)	27.0	3410.6	0.9
$[(C_5Me_5)Ir(pyridine)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (95)	19.0	3356.9	
$[(C_5Me_5)RhCl(OPPh_2)_2Pt(S_2CNEt_2)]$ (99)	59.7	3759.9	1.5
[(p-cym)$RuCl(OPPh_2)_2Pt(S_2CNEt_2)]$ (100)	61.1	3732.9	
$[(C_5Me_5)RhCl(OPPh_2)_2IrHCl$(dpae-As,As)]	56.2		1.0
[(p-cym)$RuCl(OPPh_2)_2IrHCl$(dpae-As,As)]	63.0		

TABLE 9 (continued)

	δP_E	$^1J_{PtP_E}$	δP_X	$^1J_{PtP_X}$	$J_{P_EP_X}$	OTHER
$[(C_6H_6)Ru(PPh_2Et)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (77)	44.5	3409.4	30.2		16.9	
$[(p\text{-cym})Ru(PPh_2Et)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (78)	40.7	3364.3	28.9		14.6	
$[(p\text{-cym})Ru(PPh_3)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (79)	44.4	3337.3	30.2		19.5	
$[(p\text{-cym})Ru(PC{=}C)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (83)	43.4	3361.8	26.2		14.6	
$[(p\text{-cym})Ru(dppm\text{-}P)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (84)	41.5	3364.3	31.9		14.7	-26.2^b $(38.1)^c$
$[(p\text{-cym})Ru(dppe\text{-}P)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (85)	44.2	3366.7	29.5		17.1	-14.0^b $(33.0)^d$
$[(p\text{-cym})Os(dppe\text{-}P)(SPPh_2)_2Pt(S_2CNEt_2)]Cl$ [a]	42.0	3362.3	-16.2		20.5	-13.6^b $(47.8)^d$
$[(C_6H_6)Ru(dppe\text{-}P)(SPPh_2)_2Pt(S_2CNEt_2)]Cl$ [a]	44.0	3410.6	29.4		17.1	-12.7^b $(39.1)^d$
$\{[(p\text{-cym})Ru(SPPh_2)_2Pt(S_2CNEt_2)]_2(\mu\text{-dpae})\}[PF_6]_2$	44.6	3376.5				-143.7^e $(29.4)^f$
$[(C_6H_6)Ru(S_2PMe_2)(SPPh_2)_2Pt(S_2CNEt_2)]$	37.6	3444.8	63.1		0.7	
$[(p\text{-cym})Ru(S_2PMe_2)(SPPh_2)_2Pt(S_2CNEt_2)]$	34.3	3439.9	62.7		n/m	
$[(C_5Me_5)Rh(S_2PMe_2)(SPPh_2)_2Pt(S_2CNEt_2)]$	26.6	3535.1	57.8		n/m	
$[(C_5Me_5)RhCl(OPPh_2)(SPPh_2)Pt(S_2CNEt_2)]$ (96) [k]	23.8	3669.5	54.8	3662.1	31.7	$(2.2)^g$ $(1.6)^h$
$[(p\text{-cym})RuCl(OPPh_2)(SPPh_2)Pt(S_2CNEt_2)]$ (97) [a]	28.9	3537.6	65.8	3635.2	28.3	

TABLE 9 (continued)

	δP_E	J_{PtP_E}	δP_X	J_{PtP_X}	$J_{P_EP_X}$	OTHER
$[(p\text{-cym})OsCl(OPPh_2)(SPPh_2)Pt(S_2CNEt_2)]$ (98)[a]	23.5	3540.0	61.4	3647.5	31.8	
$[(p\text{-cym})RuCl(OPPh_2)(SPPh_2)Pt(S_2CN^iPr_2)]$	30.0	3476.6	67.5	3596.2	29.3	
$[(C_5Me_5)RhCl(OPPh_2)(SPPh_2)Pt(S_2CN^iPr_2)]$	23.7	3608.4	60.6	3627.9	34.8	(2.1)[g] (1.6)[h]
$[(p\text{-cym})RuCl_2(SPPh_2)(MeOPPh_2)Pt(S_2CN^iPr_2)]$ (101)	72.3	3310.3	93.0	4096.7	24.4	
$[(p\text{-cym})OsCl_2(SPPh_2)(MeOPPh_2)Pt(S_2CN^iPr_2)]$ (102)	87.0	3339.8	95.7	4145.6	24.4	
$[(p\text{-cym})RuCl_2(SPPh_2)(MeOPPh_2)Pt(S_2CNEt_2)]$[a]	72.3	3315.4	93.3	4101.6	24.4	
$[(p\text{-cym})RuCl(SePPh_2)(PPh_2)Pt(S_2CNEt_2)]$ (104)	52.5	3809.9	28.5	2690.1	5.9	(399.0)[i]
$[(p\text{-cym})RuCl(SPPh_2)(PPh_2)Pt(S_2CNEt_2)]$ (105)[a]	74.2	3847.3	25.6	2680.5	11.0	
$[(p\text{-cym})RuCl(SePPh_2)(PPh_2)Pt(S_2CN^iPr_2)]$[a]	52.1	3784.2	27.9	2673.3	4.9	
$[(p\text{-cym})RuCl(SPPh_2)(PPh_2)Pt(S_2CN^iPr_2)]$[a]	74.6	3774.4	27.0	2653.8	9.7	
$[(C_5Me_5)RhCl(SePPh_2)(PPh_2)Pt(S_2CNEt_2)]$ (106)	40.8	3750.6	17.5	2667.0	6.7	(252.6)[i] (125.4)[j]

NOTES: a. Complex observed *in situ*; b. Dangling Phosphorus resonance; c. $^2J_{PP}$; d. $^3J_{PP}$; e $\delta P_{PF_6^-}$ f. $^1J_{PF}$; g. $^2J_{RhP_S}$; h. $^2J_{RhP_O}$; i. $^1J_{SeP}$; j. $^1J_{RhP}$; k. Run in CH_2Cl_2 with d^6-acetone lock.

TABLE 10: Hydrogen-1-n.m.r. Data for Complexes in Chapter 3. Run in $CDCl_3$ at 298°K

COMPLEX	δ_H RING FRAGMENT	δ_H $S_2CNR_2^{-a}$	PHENYL REGION	OTHERS
$[(C_6H_6)RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (71)	5.39s		7.0-7.9m	
$[(p\text{-cym})RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (72)	4.91AB 2.85sep 2.25s 1.16d[a]	3.52q 1.18t	7.1-7.8m	
$[(p\text{-cym})RuCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (74)	4.96AB 2.83sep 2.26s 1.18d[a]	4.4br 1.37d	7.1-7.8m	
$[(C_6Me_6)RuCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (75)	2.08s	4.3br 1.26d	7.0-7.9m	
$[(p\text{-cym})OsCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (76)	5.30AB 2.75sep 2.27s 1.14d[a]	3.49q 1.15t	7.2.7.6m	
$[(C_6H_6)Ru(PPh_2Et)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (77)	5.12s	3.37q 1.07t	7.0-7.7m[b]	2.40q[c] 0.68t[c]
$[(p\text{-cym})Ru(PPh_2Et)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (78)	5.22AB 1.94sep 1.65s 0.57d[a]	3.45q 1.16t	7.0-7.9m[b]	2.37q[c] 0.73t[c]
$[(p\text{-cym})OsCO(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (81)	4.77AB 2.30sep 1.89s 0.93d[a]	3.46q 1.16t	6.8-7.4m	
$[(p\text{-cym})Ru(dppm\text{-}P)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (84)	5.31AB 1.25sep 1.84s 0.38d[a]	3.45q 1.16t	6.7-7.7m[b]	3.32dd[d]
$[(C_5Me_5)RhCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (89)	1.69s	3.44q 1.10t	7.1-7.6m	
$[(C_5Me_5)IrCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (90)	1.71s	4.30br 1.28d	7.1-7.8m	
$[(C_5Me_5)RhI(SPPh_2)_2Pt(S_2CN^iPr_2)]$ (91)	1.84s	4.35br 1.31d	7.1-7.7m	
$[(C_5Me_5)Rh(py)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (94)	1.26s	3.36q 1.08t	6.8-7.6m[b]	8.54d[e]
$[(C_5Me_5)Ir(py)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (95)	1.26s	3.38q 1.10t	6.8-7.5m[b]	8.58d[e]

TABLE 11 Carbon-13-{^{1}H} n.m.r. Data for Complexes Discussed in Chapter 3 Run in $CDCl_3$ at 298°K

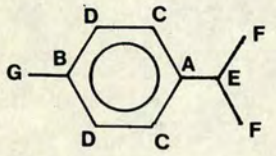
Complex[e]	δ_C Ring Fragment							δ_C $S_2CNR_2^-$		
$[(C_6H_6)RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$(71)				85.6				44.0	12.2	204.9[a]
$[(P\text{-cym})RuCl(SPPh_2)_2Pt(S_2CNEt_2)]$(72)	105.1(A)	99.4(B)	84.5(C)	81.7(D)	29.9(E)	22.1(F)	18.3(G)[b]	43.8	12.16	n/m
$[(P\text{-cym})RuCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$(74)	105.5(A)	99.7(B)	85.2(C)	82.3(D)	30.5(E)	22.3(F)	18.5(G)[b]	52.5	19.8	204.6
$[(C_6Me_6)RuCl(SPPh_2)_2Pt(S_2CN^iPr_2)]$(75)				92.7	14.9			50.4	19.8	206.2
$[(P\text{-cym})OsCl(SPPh_2)_2Pt(S_2CNEt_2)]$(76)	96.5(A)	91.4(B)	76.7(C)	73.8(D)	29.8(E)	22.4(F)	18.1(G)[b]	43.7	12.1	205.6
$[(P\text{-cym})Ru(PPh_2Et)(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$(78)[c]	114.6(A)	103.6(B)	92.0(C)	89.2(D)	29.6(E)	21.3(F)	17.2(G)[b]	44.3	12.3	202.9
$[(C_5Me_5)RhCl(SPPh_2)_2Pt(S_2CNEt_2)]$(84)				95.5[d]	8.8			43.3	12.2	206.2

Notes Table 10 a, $^3J_{HH}$ invariably 7.2Hz; b, Contains resonances attributed to BPh_4^- counterion; c, ethyl group resonance for phosphine; d, Methylene group resonance for dppm; e, High frequency α-proton resonance from pyridine ligand.

Notes Table 11 a, $^2J_{PtC}$=82.0Hz; b, Labelling of p-cymene signal; c, δ_C 21.2 and 7.6 p.p.m. tentatively proposed for ethyl group of phosphine;

d, $^1J_{RhC}$=7.3Hz

e, 121-140 p.p.m. δ_C phenyl



CHAPTER 4

THE SYNTHESIS OF PLATINUM METAL COMPLEXES CONTAINING DANGLING DIPHOSPHINE LIGANDS AND THEIR USE IN THE SYNTHESIS OF HETEROBIMETALLIC COMPLEXES

4.1 INTRODUCTION

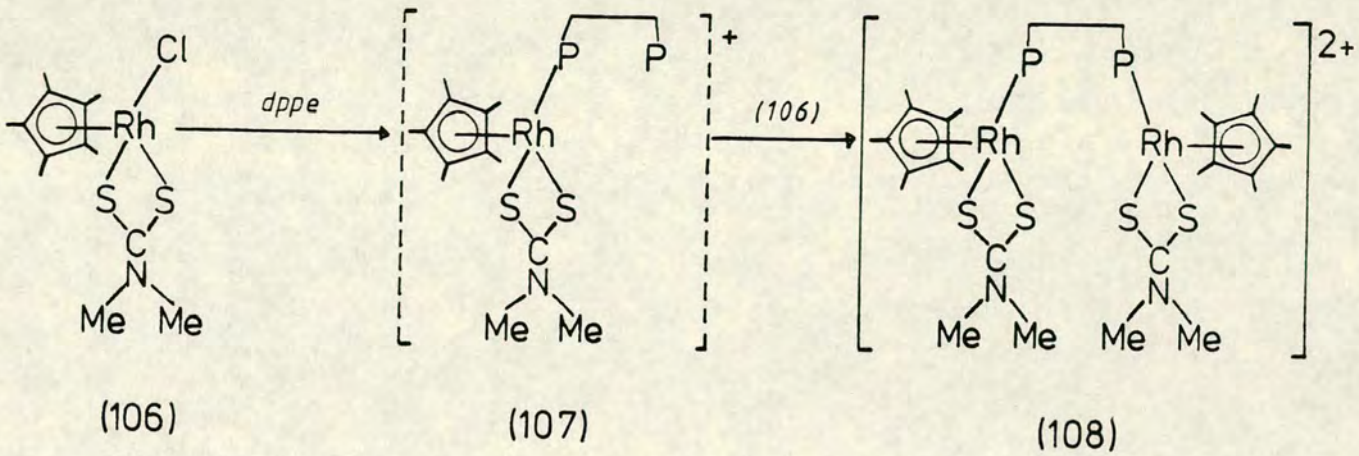
In Chapter 1 the use of complexes containing dppm ligands as precursors in the synthesis of bimetallic complexes was reviewed. Invariably, the bimetallic produced had the metal centres linked by two bridging dppm ligands. Only recently have bimetallics been prepared with a single dppm bridging ligand[187-195,216] and, with very few exceptions [196-198], these all contain a metal-metal bond and at least one strongly bridging ligand in addition to dppm. In contrast, the chemistry of the dppe ligand is principally that of a bidentate chelating ligand[42] and examples of complexes containing dangling dppe[199-204] and of dppe as a bridging ligand spanning unlike metal centres[204,205] are rare.

In this chapter, heterobimetallic complexes are prepared in which the metal centres are linked exclusively by a diphosphine bridge. A rational approach for the synthesis of these heterobimetallics was identified, which required the development of a range of monometallic complexes containing a dangling diphosphine ligand. Such complexes could then be employed as 'building-blocks' for the construction of larger heterometallic systems using the uncoordinated phosphorus atom of the diphosphine ligand to coordinate another metal fragment. Previously in Section 3.3.7, this approach was successful with the preparation of the complexes [(p-cymene)Ru(diphosphine-P)-$(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ ((84) dppm, (85) dppe) and the

construction of the tetrametallic (86) from the dppe derivative (85) . It was decided to develop monometallic complexes containing a dangling dppe ligand. It was envisaged that the techniques developed for the preparation of these complexes would also be successful for the preparation of analogous complexes containing diphosphines more noted for monodentate behaviour.

4.2 SYNTHESIS OF MONONUCLEAR COMPLEXES CONTAINING A DANGLING DIPHOSPHINE LIGAND

In 1978 Robertson and Stephenson reported the reaction of $[(C_5Me_5)Rh(S_2CNMe_2)Cl]$ (106) and dppe.[167] The metal complex was dissolved in methanol and addition of excess dppe gave a yellow solution from which a yellow solid was isolated on addition of $NaBPh_4$. On the basis of ^1H n.m.r., i.r., conductivity and microanalytical data, the yellow product was formulated as the dppe-bridged complex $\{[(C_5Me_5)Rh(S_2CNMe_2)]_2(\mu\text{-dppe})\}[BPh_4]_2$ (108) [Equation 44]. This reaction was reinvestigated in an attempt to characterise the unreported dangling-dppe intermediate $[(C_5Me_5)Rh(S_2CNMe_2)(dppe\text{-}P)]BPh_4$ (107).



(106) (107) (108)

--------[44]

The equimolar reaction of $[(C_5Me_5)Rh(S_2CNMe_2)Cl]$ (106) and dppe in CD_2Cl_2 was monitored using $^{31}P-\{^1H\}$ n.m.r. spectroscopy. The spectrum of the reaction solution revealed signals for two rhodium-diphosphine complexes and some unreacted dppe ligand. A pair of deceptively simple 'triplet' resonances appear as the A portion of a second order AA'XX' pattern (A=P, X=Rh) for the bridging-P atoms in $\{[(C_5Me_5)Rh(S_2CNMe_2)]_2(\mu\text{-dppe})\}^{2+}$ (108). The second set of signals can be assigned to the dangling-dppe complex $[(C_5Me_5)Rh(S_2CNMe_2)(dppe\text{-}P)]^+$ (107). Addition of a further quantity of (106) to the n.m.r. solution causes an increase in the intensity of the signals for (108) at the expense of the signals for (107). Continuing to add (106) leaves only the 'triplet' resonances for (108). No reaction was observed on refluxing the bridged complex (108) with a large excess of dppe in toluene for several hours. It is the stability of complex (108) which may be the driving force for its formation in the equimolar reaction of (106) and dppe described above and in the literature reaction[167] of (106) and excess dppe. If the reaction of (106) with a slight excess of dppe is carried out under mild conditions (CH_2Cl_2, high dilution, 0°C), pure samples of the dangling-dppe complex (107) can be isolated. Even using mild conditions, the first and major product precipitated on addition of methanolic $NaBPh_4$ to the reaction solution, is the bridged complex (108). On careful work-up of the golden-yellow filtrate, after removal of (108), the dangling-dppe complex (107) can be recovered in 15% yield. Over

a period of 24 hours in $CDCl_3$ solution the complex (107) decomposes to give a single product showing an ABX pattern in the $^{31}P-\{^1H\}$ n.m.r. spectrum. This could indicate formation of the phosphine oxide complex $[(C_5Me_5)Rh(S_2CNMe_2)(Ph_2P(CH_2)_2P(O)Ph_2)]BPh_4$ by air oxidation of the dangling P atom in (107). Further work involving chemical oxidation of the dangling P atom is required to confirm this assignment.

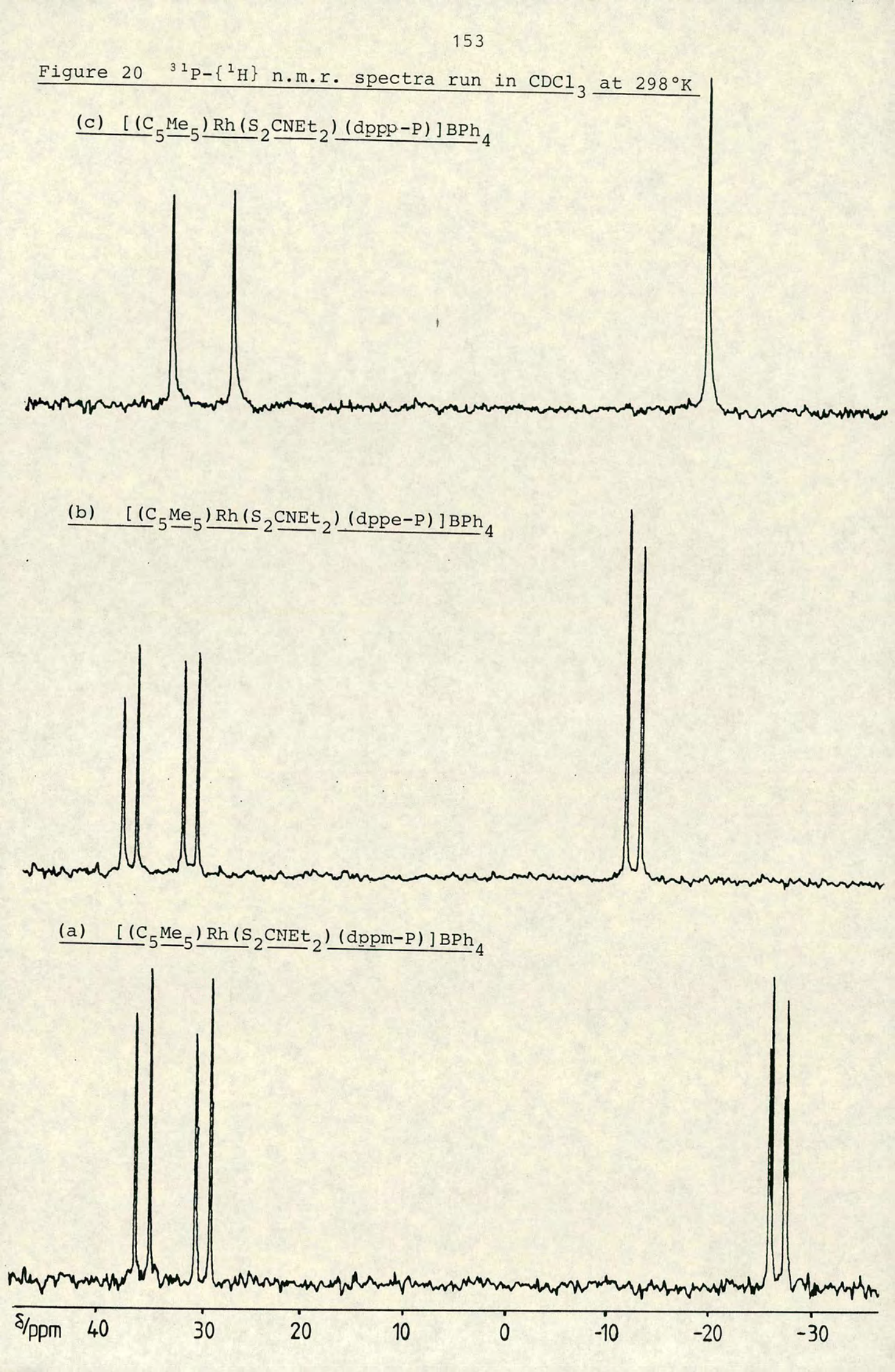
Remarkably, the equimolar reaction of $[(C_5Me_5)Rh(S_2CNEt_2)Cl]$ and dppe in chloroform gives on addition of methanolic $NaBPh_4$ the stable (over two weeks in $CDCl_3$ solution) dangling-dppe complex $[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (109) as an orange microcrystalline solid in 85% yield. The $^{31}P-\{^1H\}$ n.m.r. spectrum of (109) [Figure 20(b)] run in $CDCl_3$ at 298°K shows a doublet of doublets for the P bound to Rh (δP 34.1 p.p.m., $^1J_{RhP}$ 145.9, $^3J_{PP}$ 34.2Hz) and a doublet, close to the resonance position for free dppe, for the dangling P atom (δP -12.3 p.p.m.). On high resolution a further doublet splitting due to long range Rh coupling is detected on the low frequency doublet ($^4J_{RhP}$ 0.4Hz). The ^1H n.m.r. spectrum of (109) consists of a doublet resonance for the C_5Me_5 ring ($\delta C_5\underline{Me}_5$ 1.32 p.p.m., $^4J_{PH}$ 3.2Hz) indicative of one P bound at Rh. The ethyl groups of the dithiocarbamate ligand appear as a triplet ($\delta_{CH_2\underline{CH}_3}$ 1.06 p.p.m.) and a complex resonance derived from an ABM_3 spin system ($\delta_{\underline{CH}_2CH_3}$ centred at 3.39 p.p.m.). Two broad multiplets appear for the methylene groups of the dppe ligand ($\delta_{\underline{CH}_2}$ 1.84, 2.44 p.p.m.) with the lower

Figure 20 $^{31}P-\{^{1}H\}$ n.m.r. spectra run in $CDCl_3$ at 298°K

(c) $[(C_5Me_5)Rh(S_2CNEt_2)(dppp\text{-}P)]BPh_4$

(b) $[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]BPh_4$

(a) $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$

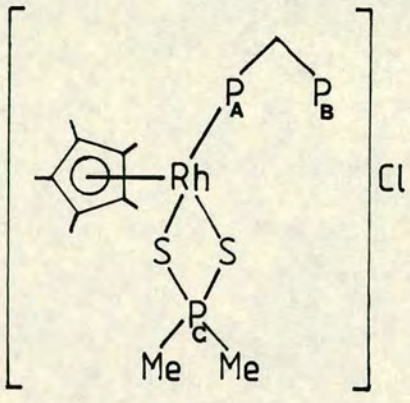


frequency signal assigned to the protons nearest the uncoordinated P atom. Lastly, in the region 7.0-7.7 p.p.m. are signals associated with the phenyl protons of the BPh_4^- ion and the dppe ligand. Conductivity (1:1 electrolyte in nitromethane), i.r. (ν_{CN} 1516 cm^{-1}) and analytical data provide further evidence to support the formulation (109).

The equimolar reaction of $[(C_5Me_5)Rh(S_2CNEt_2)Cl]$ and dppm in chloroform followed by addition of methanolic $NaBPh_4$ allows the recovery of the orange, dangling-dppm complex $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (110) [Figure 20(a)], like that of the dppe analogue (109), is characteristic of one P bound to Rh (d of d, δP 32.2 p.p.m., $^1J_{RhP}$ 146.5, $^2J_{PP}$ 35.4Hz) with one P dangling (d of d, δP -26.8 p.p.m., $^3J_{RhP}$ 3.7Hz). The ^1H n.m.r. spectrum shows the C_5Me_5 resonance as a doublet ($\delta_{C_5Me_5}$ 1.34 p.p.m., $^4J_{PH}$ 3.3Hz) with line narrowing revealing a further doublet coupling ($^3J_{RhH}$ 0.3Hz). In the methylene region, a complex multiplet derived from an ABM_3 spin system is observed for the diethyldithiocarbamate ligand ($\delta_{C\underline{H}_2CH_3}$ centred at 3.41; $\delta_{CH_2C\underline{H}_3}$ tiplet at 1.0 p.p.m.) and the methylene resonance for the dppm ligand appears as a pseudo doublet ($\delta_{C\underline{H}_2}$ 3.10 p.p.m.). $^{13}C\text{-}\{^1H\}$ n.m.r., i.r., conductivity and analytical evidence also supports formation of the dangling-dppm complex (110).

Similarly the equimolar reaction of $[(C_5Me_5)Rh(S_2CNEt_2)Cl]$ and either dppp ($Ph_2P(CH_2)_3PPh_2$) or dmpe ($Me_2P(CH_2)_2PMe_2$)

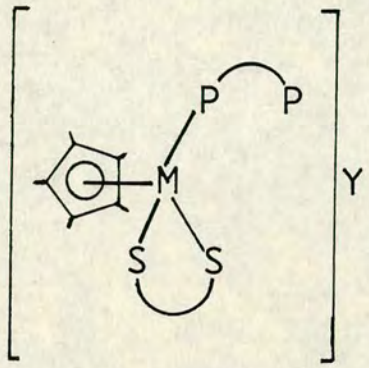
allows recovery of the dangling-diphosphine derivatives $[(C_5Me_5)Rh(S_2CNEt_2)(dppp\text{-}P)]BPh_4$ (111) [see Figure 20(c)] and $[(C_5Me_5)Rh(S_2CNEt_2)(dmpe\text{-}P)]BPh_4$ (112). In addition, the reaction of $[(C_5Me_5)Ir(S_2CNEt_2)Cl]$ with either dppm or dppe gives for dppm the complex $[(C_5Me_5)Ir(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (113) and for dppe gives a mixture of the dangling and bridging complexes $[(C_5Me_5)Ir(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (114) and $\{[(C_5Me_5)Ir(S_2CNEt_2)]_2(\mu\text{-dppe})\}[BPh_4]_2$. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra for (113) and (114) run in $CDCl_3$ at 298°K both show a doublet for the P bound to Ir ((113) δP -1.9, $^2J_{PP}$ 40.3; (114) δP 0.2 p.p.m., $^3J_{PP}$ 35.9Hz) and a related doublet for the dangling P atom ((113) δP -27.9; (114) δP -12.5 p.p.m.). The equimolar reaction of $[(C_5Me_5)Rh(S_2PMe_2)Cl]$ with either dppm or dppe in $CDCl_3$ produces the dangling diphosphine complexes $[(C_5Me_5)Rh(S_2PMe_2)(dppm\text{-}P)]Cl$ (115) and $[(C_5Me_5)Rh(S_2PMe_2)(dppe\text{-}P)]Cl$ (116). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra for (115) and (116) contain valuable coupling constant information. For example, in the spectrum of (115) one, two and three bond J_{RhP} coupling constants can be measured.



(115)

δP_A	31.5 ppm	$^1J_{RhP_A}$	145.1Hz
δP_B	-26.4 ppm	$^3J_{RhP_B}$	4.4Hz
δP_C	101.2 ppm	$^2J_{RhP_C}$	10.0Hz
$^2J_{P_AP_B}$	30.8Hz	$^3J_{P_AP_C}$	12.1Hz

Finally, the ruthenium complex $[(C_6H_6)Ru(S_2PPh_2)$-(dppe-P)]Cl (117) can be prepared by the equimolar reaction of $[(C_6H_6)Ru(S_2PPh_2)Cl]$ and dppe in $CDCl_3$.



(109-116)

M	S S	P P
Rh	$S_2CNEt_2^-$	(110) dppm (109) dppe
		(111) dppp (112) dmpe
Ir	$S_2CNEt_2^-$	(113) dppm (114) dppe
Rh	$S_2PMe_2^-$	(115) dppm (116) dppe

An X-ray structure determination was carried out on single crystals of the complex $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]$-$BPh_4$ (110) to unequivocally establish the dangling coordination mode for the dppm ligand and also, by implication, the dangling coordination mode for the diphosphine ligand in complexes (107) and (109-117). The structure of the cation $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]^+$ [Figure 21] confirms that the diphosphine ligand uses one P donor atom to coordinate to the Rh atom leaving the other P donor atom dangling. The Rh coordination sphere is completed by the η^5-pentamethylcyclopentadienyl ligand and the two S atoms of the chelating dithiocarbamate ligand. The Rh-P(1) (2.315(2)Å), Rh-S (2.369(2) and 2.373(3)Å) and the Rh-C (2.201(8)-2.232(8)Å) bond distances are similar to those found in

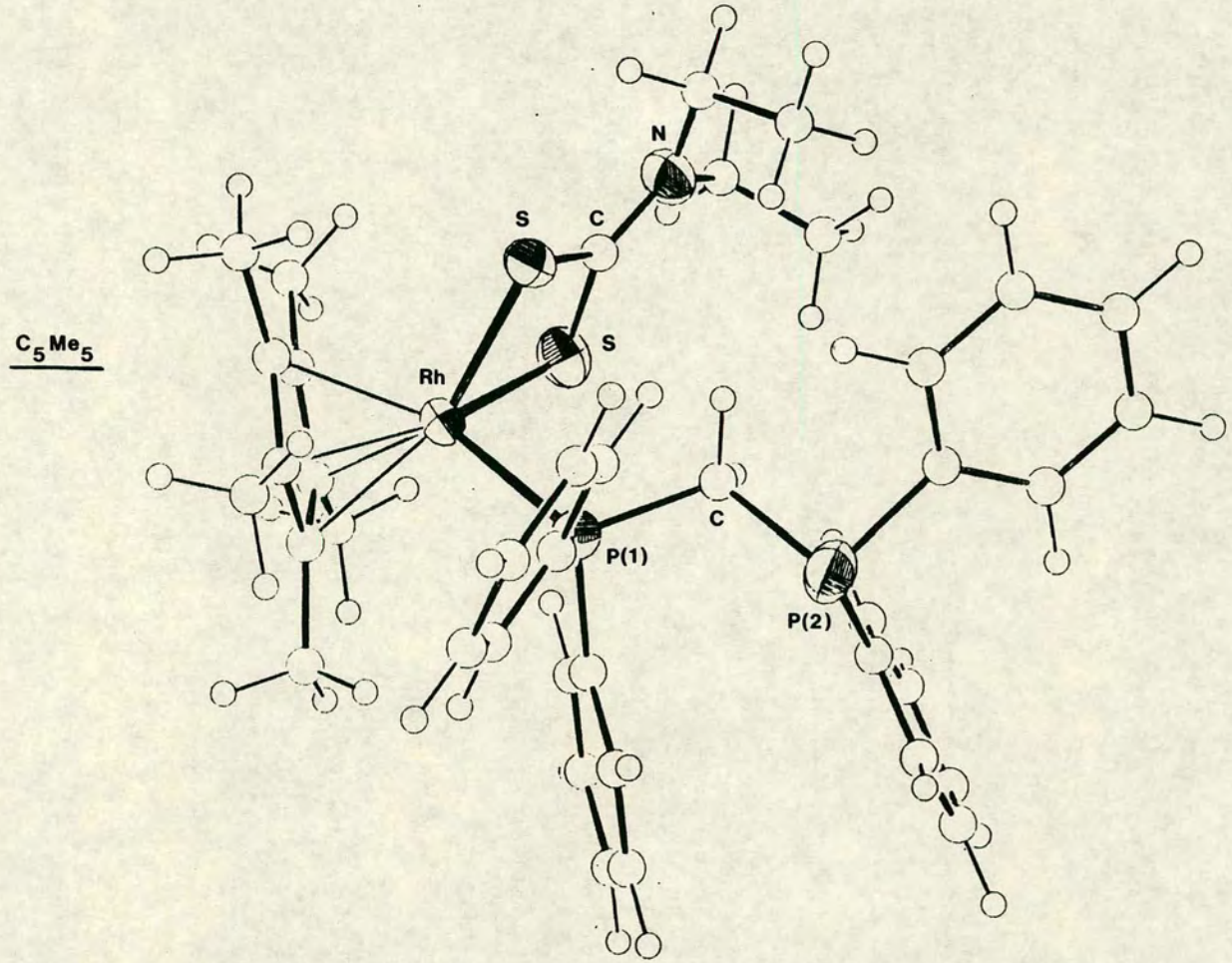


Figure 21 The molecular structure of the cation $[(C_5Me_5)Rh(S_2CNEt_2)-(dppm-P)]^+$ (110)

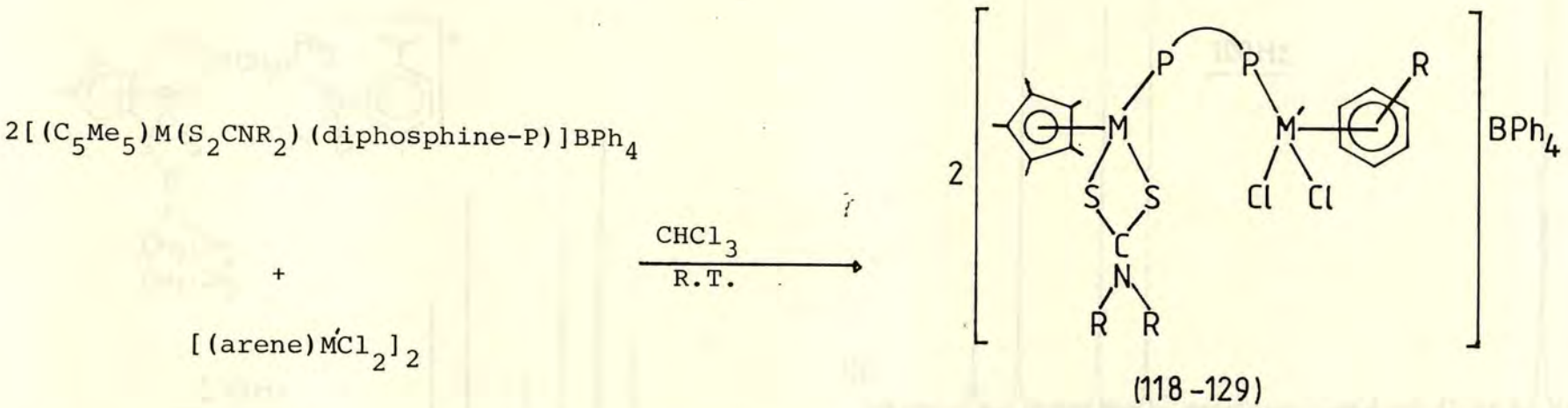
the dppe-bridged complex $\{[(C_5Me_5)Rh(S_2CNEt_2)]_2(\mu\text{-dppe})\}[BPh_4]_2$ (Rh-P 2.300(2); Rh-S 2.349(2) and 2.364(2); Rh-C 2.179(6)-2.228(7)Å) also characterised during this work.[206] The $\hat{PCP}$ bond angle of 115.2(4)° in (110) is slightly distorted from the tetrahedral angle but falls typically within the range of $\hat{PCP}$ bond angles found in the few other structurally characterised examples of complexes containing a dangling dppm ligand (trans-$Pd(Bu^tNC)_2(dppm\text{-}P)_2]^{2+}$, $\hat{PCP}$ 111.7(6)°;[207] $[(C_5H_5)RhCO(dppm\text{-}P)]$, 114.4(4)°[208]; $[MoCl_2(CO)_2(dppm\text{-}P,P)(dppm\text{-}P)]$ 116.0°;[209] $[Pt_2H(\mu\text{-}dppm)_2(dppm\text{-}P)]^+$ 117.6°;[210] $[Ru(TPP)(dppm\text{-}P)_2]$ 118.7(6)°[211]). A torsional angle of 178.8(3)° for Rh-P(1)-C(1)-P(2) reveals that this unit is almost trans. The bond angles around the uncoordinated P(2) atom (C(1)-P(2)-C(31) 99.2(4)°, C(1)-P(2)-C(41) 102.2(3)°; C(31)-P(2)-C(41) 103.3(3)°) suggest that the lone pair of electrons are available to function as a donor set toward suitable substrates.

4.3 THE RATIONAL SYNTHESIS OF HETEROBIMETALLIC COMPLEXES

In this section, the rhodium and iridium dangling diphosphine complexes prepared in Section 4.2 are used in the synthesis of a range of heterometallic compounds. The uncoordinated phosphorus atom in $[(C_5Me_5)M(S_2CNR_2)(diphosphine\text{-}P)]BPh_4$ (110-114) is sufficiently basic to bridge-cleave $[(arene)MCl_2]_2$ (M = Ru, arene = C_6H_6, p-cymene, C_6Me_6; M = Os, arene = p-cymene) to produce heterobimetallic

complexes of the type $[(C_5Me_5)M(III)(S_2CNR_2)(\mu\text{-diphosphine})\text{-}M(II)Cl_2(arene)]BPh_4$ (118-129) in which the metal centres are linked by a single diphosphine bridge [Scheme 15].

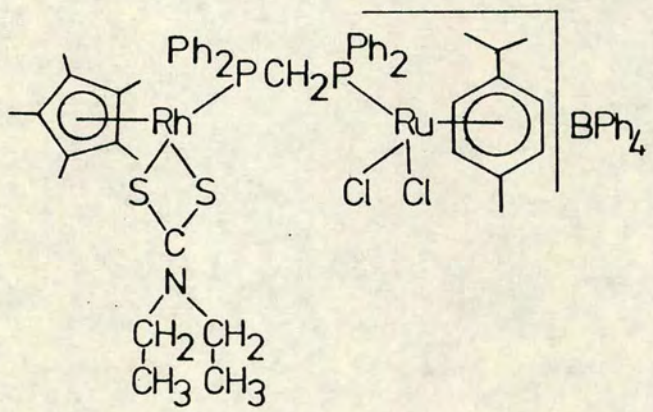
Treatment of $[(p\text{-cym})RuCl_2]_2$ with two equivalents of $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110) in $CDCl_3$ at 298°K results in the immediate formation of the heterobimetallic complex $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(p\text{-cym})]BPh_4$ (118). A comparison of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra for (110) and the product (118) [Figure 22(a)] shows that the resonance assigned to the dangling P atom in (110) (δP -26.8 p.p.m.) is replaced for the product (118) by a resonance in the region associated with P bound to Ru (δP 23.0 p.p.m.). As a result of increasing the spectrometer operating frequency [see insert (b), Figure 22], the spectrum of (118) changes from a second order ABX pattern to essentially a first order pattern with separate resonances observed for P bound to Rh (δP 29.9 p.p.m., $^1J_{RhP}$ 144.4, $^2J_{PP}$ 52.3Hz) and P bound to Ru (δP 23.0 p.p.m., $^3J_{RhP}$ 4.4Hz). The ^1H n.m.r. spectrum of (118) [Figure 23] consists of signals for the C_5Me_5 ring ($\delta_{C_5\underline{Me}_5}$ 1.27d(15), $^4J_{PH}$ 3.2Hz); the p-cymene ring ($\delta_{C\underline{H}_3}$ 1.58s(3), $\delta_{CH(CH_3)_2}$, 0.85d(6), 2.23sep(1), $^3J_{HH}$ 6.9Hz, $\delta_{C_6\underline{H}_4}$ 4.98AB(4), J_{HH} 6.3Hz, $\Delta\delta$9.2Hz); the ethyl groups of the dithiocarbamate ligand ($\delta_{CH_2CH_3}$ 1.11t(6), 3.95(4) centre ABM_3, $^3J_{HH}$ 7.2Hz); the methylene group of the dppm ligand (δ_{CH_2} 4.18 'dd'(2)) and the phenyl groups of the BPh_4^- ion and the dppm ligand ($\delta_{C_6H_5}$ 6.8-7.5 p.p.m. (40)). A conductivity study in nitromethane confirmed (118) as a 1:1 electrolyte (slope of $\Lambda_\infty\text{-}\Lambda_e$ against $c_e^{\frac{1}{2}}$ graph of 296) and



$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(p\text{-cym})]BPh_4$	(118)	$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})OsCl_2(p\text{-cym})]BPh_4$	(124)
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})RuCl_2(p\text{-cym})]BPh_4$	(119)	$[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(p\text{-cym})]BPh_4$	(125)
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppp})RuCl_2(p\text{-cym})]BPh_4$	(120)	$[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(C_6Me_6)]BPh_4$	(126)
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dmpe})RuCl_2(p\text{-cym})]BPh_4$	(121)	$[(C_5Me_5)Rh(S_2CNMe_2)(\mu\text{-dppe})RuCl_2(p\text{-cym})]BPh_4$	(127)
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RhCl_2(C_6H_6)]BPh_4$	(122)	$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})RuCl_2(C_6Me_6)]BPh_4$	(128)
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(C_6Me_6)]BPh_4$	(123)	$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})OsCl_2(p\text{-cym})]BPh_4$	(129)

Scheme 15: Preparation of the complexes $[(C_5Me_5)M(S_2CNR_2)(\mu\text{-diphosphine})M'Cl_2(arene)]BPh_4$ (118-129)

Figure 23 The ^{1}H n.m.r. spectrum of $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})\text{-}RuCl_2(p\text{-cymene})]BPh_4$ (118) in $CDCl_3$ at 298°K



the i.r. spectrum of the isolated red product revealed ν_{CN} 1512, ν_{RuCl} 288, 278 and prominent bands at 700 and 730 cm^{-1} for the BPh_4^- ion. Positive ion FAB mass spectral (parent cation 1077 m/e) and microanalytical data are also consistent with the proposed formulation (118).

A series of singly bridged dppm heterobimetallics have been prepared in which either the metals or the arene ring bound at ruthenium are varied.[212] Treatment of either $[(C_6H_6)RuCl_2]_2$ or $[(C_6Me_6)RuCl_2]_2$ with two equivalents of $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110) in chloroform at 298°K produces the complexes $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})\text{-}RuCl_2(arene)]BPh_4$ ((122) C_6H_6; (123) C_6Me_6) and using $[(p\text{-cym})OsCl_2]_2$ and (110) the complex $[(C_5Me_5)Rh(S_2CNEt_2)\text{-}(\mu\text{-dppm})OsCl_2(p\text{-cym})]BPh_4$ (124) can be produced. Similarly the complexes $[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(arene)]BPh_4$ ((125) p-cymene; (126) C_6Me_6) can be prepared using $[(C_5Me_5)Ir(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (113) and either $[(p\text{-cym})RuCl_2]_2$ or $[(C_6Me_6)RuCl_2]_2$. The complexes (122-126) have been fully characterised by elemental analysis, i.r., ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. In addition, the structure of $[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(C_6Me_6)]\text{-}BPh_4$ (126) has been confirmed by a single crystal X-ray diffraction study. The cation [Figure 24] shows the Ir and Ru metal centres linked by a single dppm bridging ligand. In the absence of a metal-metal bond and/or an additional bridging ligand to constrain the metal centres in close proximity, as for example in the complexes $[Br_2Pt(\mu\text{-dppm})(\mu\text{-CO})Fe(CO)_3]$, Pt-Fe 2.647(4);[188] $[(PPh_3)Pt(\mu\text{-dppm})(\mu\text{-CO})Fe(CO)_3]$,

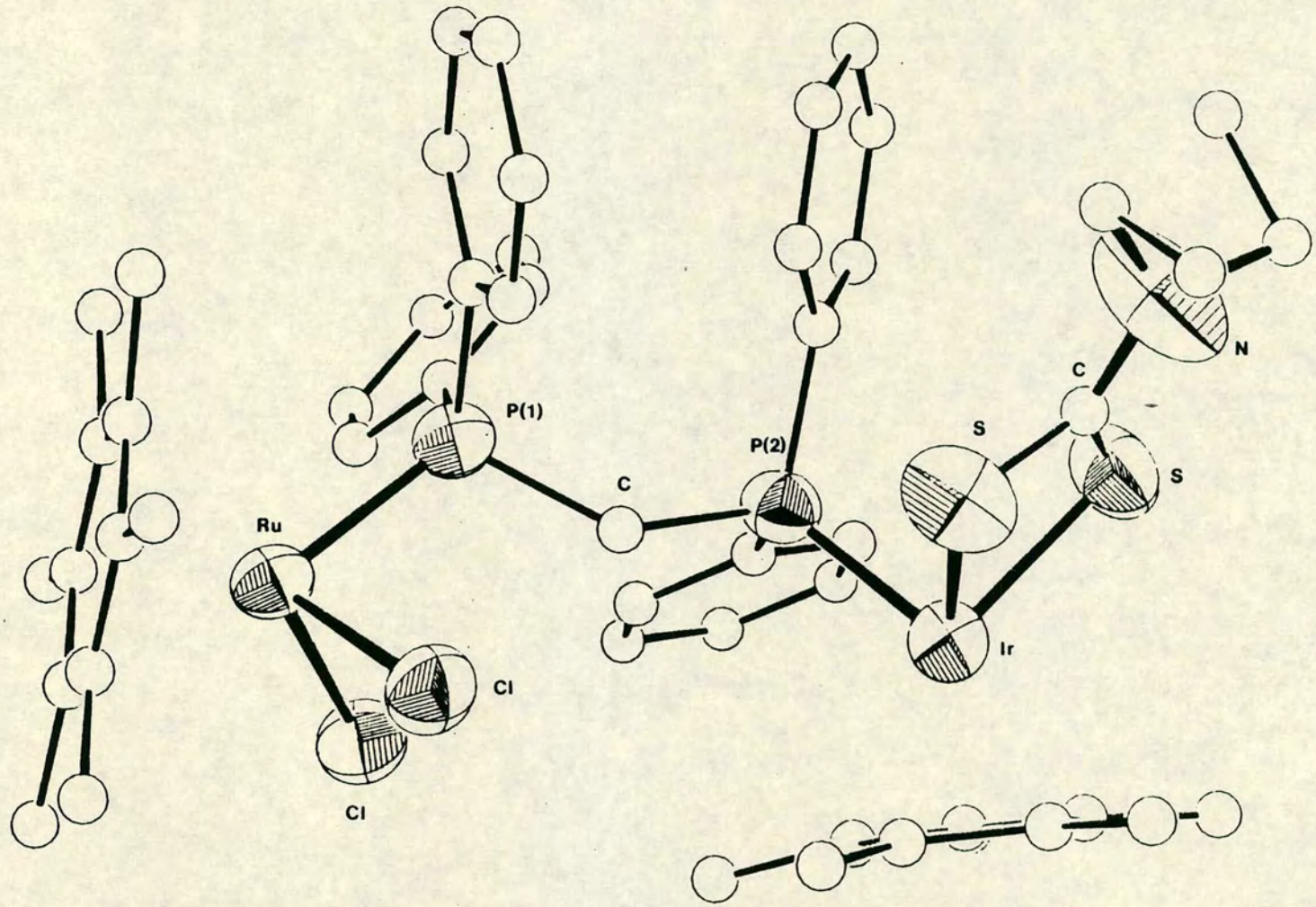


Figure 24 The molecular structure of the cation $[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(C_6Me_6)]^+$ (126)

Pt-Fe 2.579(4)[191] and $[Rh_2(C_5H_5)_2(\mu\text{-CO})(\mu\text{-dppm})]$, Rh-Rh 2.683(1)Å,[187] the Ir and Ru centres are located 6.640(2)Å apart. The $P\hat{C}P$ bond angle is distorted significantly from the tetrahedral angle at 133.1(9)° with the non-bonded P···P distance calculated as 3.385Å. This compares with $P\hat{C}P$ bond angles of between 111.7 and 118.7° and non-bonded P·····P distances of generally about 3.1Å found for complexes containing a dangling dppm ligand[207-211] and suggests that the distortion of the $P\hat{C}P$ bridging unit in (126) is necessary to accommodate the two bulky metal-ligand fragments. During the course of this work the homobimetallic complex $\{[(C_5H_5)Ru(1,10\text{-phen})]_2(\mu\text{-dppm})\}[PF_6]_2$ was structurally characterised.[198] This structure also revealed a large M·····M separation (6.445(1)Å) and $P\hat{C}P$ bond angle (133.1(3)°). In (126) the Ru coordination sphere is completed by two chlorine atoms and a $\eta^6\text{-}C_6Me_6$ arene ring. The Ru-P (2.359(5)Å) and Ru-Cl (2.407(5), 2.417(5)Å) bond distances and $Cl\hat{R}uCl$ (86.6(2)) and $Cl\hat{R}uP$ (85.7(2) and 87.8(2)°) bond angles are comparable with the corresponding values found for the monophosphine complexes $[(arene)RuCl_2PPh_2Me]$ (arene = C_6H_6, p-cymene),[213] while Ru-C distances are in the range 2.208-2.245(11)Å. The Ir coordination sphere is completed by a $\eta^5\text{-}C_5Me_5$ ring and two S atoms of the chelating dithiocarbamate ligand. The Ir-P (2.300(5)Å), Ir-S (2.376(6) and 2.380(6)Å) and Ir-C (2.196-2.217(13)Å) bond distances are well within the limits for these atom pairs. Interestingly, a comparison of the $^2J_{PP}$ coupling constants for the dangling-dppm complexes ((110) $^2J_{PP}$ 35.4; (113) 40.3Hz) and the heterobimetallics constructed from them ((118, 122-126)

$^2J_{PP}$ 50.1-52.7Hz) reveals a significant increase in this parameter. If the results from solid state studies are representative of solution behaviour then the increase in $^2J_{PP}$ coupling constant may be a result of altering the PĈP bond angle on changing the dppm ligand mode from dangling ($[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]^+$ PĈP 115.2(4)°) to being the sole briding ligand ($[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6Me_6)]^+$ PĈP 133.1(9)°).

The facile reaction of the dangling-diphosphine complexes $[(C_5Me_5)Rh(S_2CNEt_2)(diphosphine\text{-}P)]BPh_4$ (diphosphine = dppe (109), dppp (111), dmpe (112)) with 0.5 molar equivalents of $[(p\text{-}cym)RuCl_2]_2$ in $CDCl_3$ at room temperature produces the heterobimetallics $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}diphosphine)RuCl_2(p\text{-}cym)]BPh_4$ (diphosphine = dppe (119), dppp (120), dmpe (121)), which are the single-bridging dppe, dppp and dmpe analogues of (118). Under similar conditions, treatment of (109) with 0.5 molar equivalents of either $[(C_6Me_6)RuCl_2]_2$ or $[(p\text{-}cym)OsCl_2]_2$ produces the heterobimetallics $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)RuCl_2(C_6Me_6)]BPh_4$ (128) and $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)OsCl_2(p\text{-}cym)]BPh_4$ (129) respectively. The heterobimetallics (119-121, 127-130) have been characterised on the basis of $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy and in some cases macroanalytical and i.r. data.

A preliminary investigation into the chemistry of the heterobimetallic complex $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(p\text{-}cym)]BPh_4$ (118) was directed toward substitution of the chloride ligands on ruthenium by PR_3, CO and CH_3CN ligands. Limited success was achieved on stirring (118) with a slight

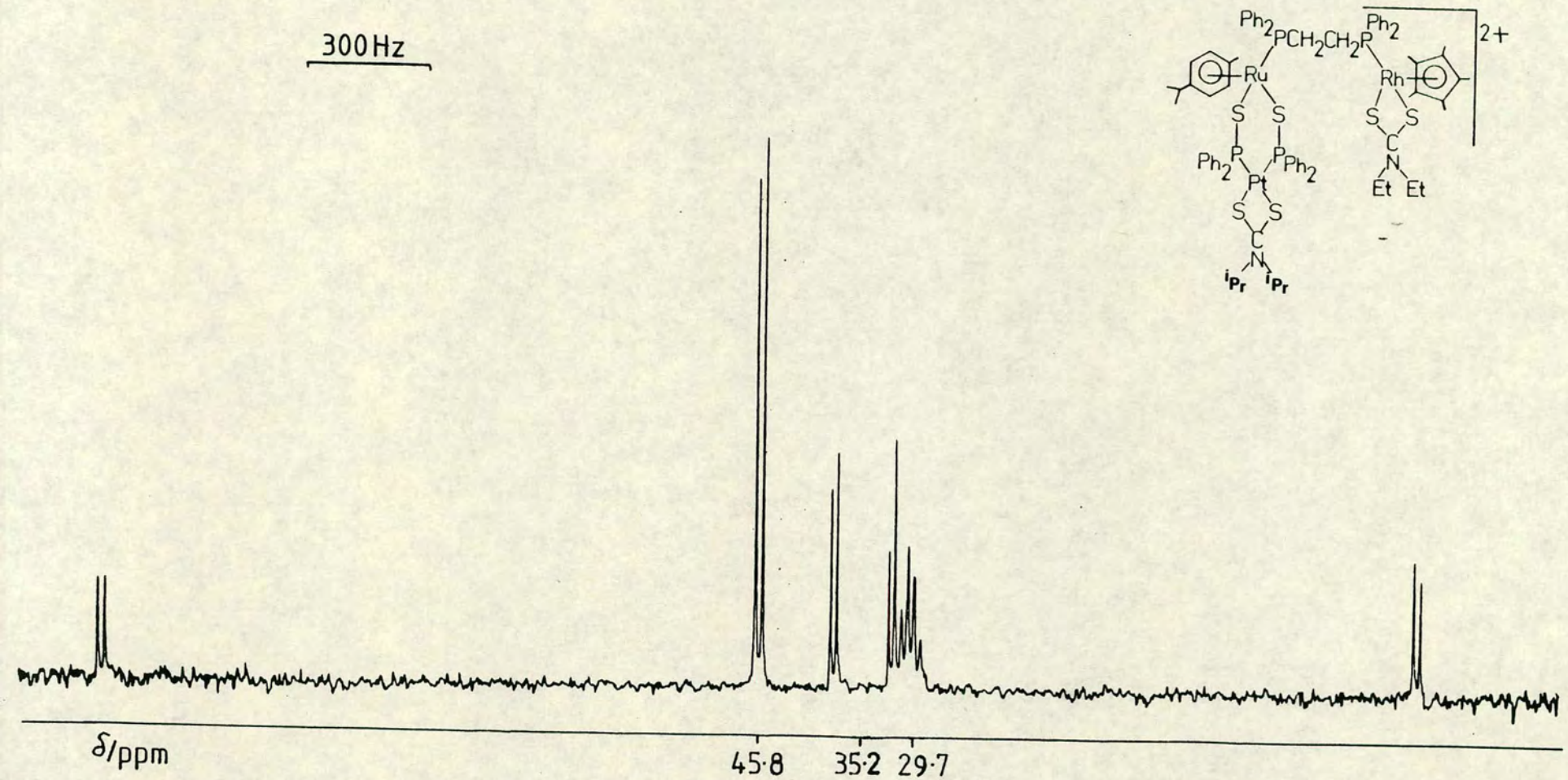
molar excess of $PPhMe_2$ in a mixed $CHCl_3$/MeOH solvent in the presence of $NaBPh_4$ to produce the complex $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RuCl(PPhMe_2)(p\text{-cym})][BPh_4]_2$ (133); identified as the minor component in a mixture with (118) by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. (A better route to the complex (133) would almost certainly be to treat $[(C_5Me_5)Rh(S_2CNEt_2)Cl]$ with an equimolar quantity of $[(p\text{-cym})Ru(PPhMe_2)(dppm\text{-}P)Cl]BPh_4$ (143) in $CDCl_3$). No reaction was observed on treating (118) at ambient temperature with either CO in $CDCl_3$ in the presence of $TlBF_4$ or $TlBF_4$ in CH_3CN.

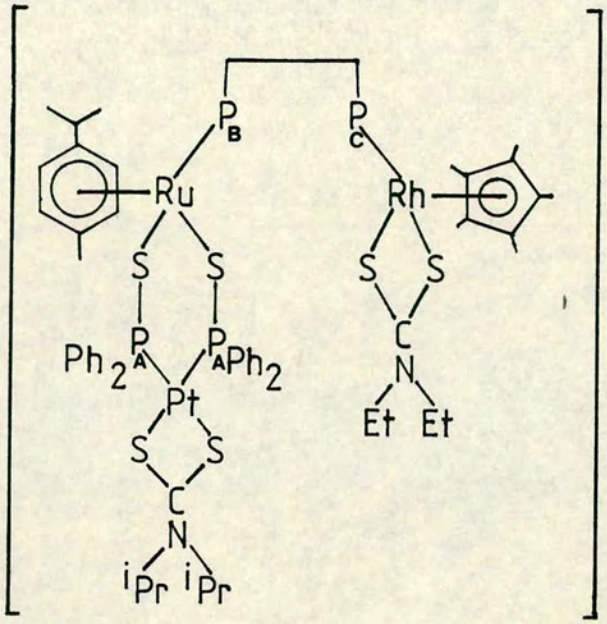
It has been reported that in non-polar solvents a wide variety of monodentate ligands L, including tertiary phosphines, react to bridge-cleave $[CODIrCl]_2$ (35) to give neutral complexes of the type [CODIrClL].[214] It was anticipated that the use of dangling-diphosphine complexes in reaction with $[CODIrCl]_2$ would provide a route to a new range of heterobimetallic complexes. This was indeed the case. Reaction of $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110) with $[CODIrCl]_2$ in $CDCl_3$ in a respective 2:1 molar ratio produced a single product which was identified <u>in situ</u> by $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy as the heterobimetallic complex $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})IrCl(COD)]BPh_4$ (131). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the reaction solution displays the requisite pair of doublet of doublet resonances for (131) with the chemical shift positions indicative of P bound to Rh (δP 30.0 p.p.m., $^1J_{RhP}$ 145.6Hz, $^2J_{PP}$ 38.0Hz) and P bound to Ir (δP 13.6 p.p.m., $^3J_{RhP}$ 3.9Hz). Most

notably the ^{1}H n.m.r. spectrum of the reaction solution reveals separate resonances for the alkene protons trans to P ($\delta_{C\underline{H}}$ 5.0 p.p.m.) and trans to Cl ($\delta_{C\underline{H}}$ 2.27 p.p.m.) in the 1,5-COD ligand. In addition, the resonance position for the methylene protons ($\delta_{C\underline{H}_2}$) of the dppm ligand shifts from 3.1 p.p.m. in the complex (110) to 4.27 p.p.m. which, when compared with the ^{1}H n.m.r. data for the heterobimetallic complexes (118, 119, 122-126), is consistent with the dppm adopting a bridging coordination mode. After four hours in $CDCl_3$ solution some product decomposition was apparent with the growth of several new signals including signals at 5.6 and 2.3 ppm for free 1,5-COD. Attempts to recover the product by adding methanol to the reaction solution resulted in extensive decomposition. The dppe-bridged analogue $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})IrCl(COD)]BPh_4$ (132) was prepared by mixing $[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (109) and $[CODIrCl]_2$ in a 2:1 molar ratio in $CDCl_3$ and was characterised <u>in situ</u> by $^{31}P\text{-}\{^{1}H\}$ n.m.r. spectroscopy.

Finally, the heterobimetallic complex $[(p\text{-cym})RuCl(SPPh_2)_2Pt(S_2CN^{i}Pr_2)]$ (74), previously shown in Chapter 3 to undergo substitution reactions at the chloride site, was treated with an equimolar quantity of $[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (109) in $CDCl_3$ at room temperature. The $^{31}P\text{-}\{^{1}H\}$ n.m.r. spectrum of the reaction solution [Figure 25] indicated that an immediate reaction had taken place with the uncoordinated P atom of the diphosphine ligand in (109) substituting for the chloride ligand in (74) to form the heterotrimetallic complex (134).

Figure 25 The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $\{[(p\text{-cymene})Ru(SPPh_2)_2Pt(S_2CN^iPr_2)]-(\mu\text{-dppe})Rh(S_2CNEt_2)(C_5Me_5)\}[BPh_4]_2$ (134) in $CDCl_3$ at 298°K





(134)

δP_A	45.8 ppm
δP_B	29.7 ppm
δP_C	35.2 ppm
$^1J_{PtP_A}$	3320.3Hz
$^1J_{RhP_C}$	146.5Hz
$^3J_{P_AP_B}$	17.6Hz
$^3J_{P_BP_C}$	14.6Hz

The product (134) was recovered as a light red solid on addition of methanolic $NaBPh_4$ to the reaction solution. Further, consistent evidence for the product (134) was obtained by ^1H n.m.r. and i.r. spectroscopy and microanalysis.

4.4 CONCLUSIONS

A rational and relatively straightforward route has been devised for the preparation of a wide range of heterobimetallic complexes. The route uses mononuclear complexes containing a single, dangling diphosphine ligand which act as exotic 'tertiary phosphine ligands' during reaction. It is anticipated that the 'phosphine-metal' ligands could replace the ubiquitous tertiary phosphine ligand in many of the reactions encountered in Coordination Chemistry to produce new heterobimetallic systems. The lack of an easily generated active site on the metal in the 'phosphine-metal' complexes does however restrict the reactivity of any bimetallic complex formed. The work presented in Sections 5.1 to 5.5 of Chapter 5 was an attempt to produce more reactive bimetallic systems.

4.5 EXPERIMENTAL

4.5.1 MATERIALS

The complexes $[(arene)MCl_2]_2$ (M = Ru, arene = C_6H_6, p-cymene, C_6Me_6; M = Os, arene = p-cymene), $[(C_5Me_5)MCl_2]_2$ (M = Rh, Ir), $[CODIrCl]_2$, $[(C_5Me_5)Rh(S_2CNMe_2)Cl]$, $[(C_5Me_5)Rh(S_2PMe_2)Cl]$ and $[(C_6H_6)Ru(S_2PPh_2)Cl]$ were prepared by standard literature methods[97,141,188]. The diphosphines were obtained from commercial sources.

4.5.2 Crystal data for $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110)

$C_{44}H_{47}NS_2P_2Rh.C_{24}H_{20}B$, M = 1090, triclinic.
a = 10.428(4), b = 15.452(8), c = 19.416(9), α = 107.8(4),

β = 90.41(4), γ = 105.92(4), U = 2849Å^3, Z = 2, D_c 1.271 g cm^{-3}, Space group $P\bar{1}$ (No.2) Mo-K_α radiation λ = 0.71069Å, MU 4.27 cm^{-1}, F(000) = 1144, T = 298°K. The structure solution and refinement were based on 4612 observed (I>6σ(I)) reflections (7132 measured) from a Stoe-stadi 2 diffractometer to give final R and R_w values of 0.0534 and 0.0712 respectively.

Crystal data for $[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(C_6Me_6)]$-$BPh_4.CHCl_3$ (126)

$C_{52}H_{65}NS_2P_2Cl_2RuIr.BC_{24}H_{20}.CHCl_3$, M = 1632.97, Monoclinic. a = 35.815(17), b = 12.378(6), c = 40.569(19)Å, β = 124.718(28)°, U = 14783Å^3, Z = 8, D_c = 1.467 g cm^{-3}, Space group $C_{2/c}$ (No.15), Mo-K_α radiation λ = 0.71069Å, MU 23.12 cm^{-1}, F(000) = 6624, T = 298°K. The structure solution and refinement were based on 4319 observed (I>6σ(I)) reflections (10091 measured) from a Stoe-Siemens AED2 diffractometer to give final R and R_w values of 0.0569 and 0.0739 respectively.

4.5.3 METAL COMPLEXES PREPARED IN CHAPTER 4

$[(C_5Me_5)Rh(S_2CNEt_2)Cl]$ $[(C_5Me_5)RhCl_2]_2$ (0.358 g, 0.58 mmol) was stirred with $NaS_2CNEt_2.3H_2O$ (0.261 g, 1.16 mmol) in CH_3CN (55 ml) for 3 hours. The reaction solution was filtered through celite to remove NaCl and the filtrate reduced to dryness. The crude product was dissolved in $CHCl_3$ (3 ml) and diethylether added to precipitate the dark red product which was collected by filtration, washed

with cold Et_2O and dried *in vacuo* at 56°C. Yield 0.4 g, 82%. Found, C 42.4, H 6.01, N 3.35; Calc. for $C_{15}H_{25}NS_2ClRh$, C 42.7, H 5.97, N 3.32. ^1H n.m.r. $CDCl_3$/ 298°K $\delta_{C_5Me_5}$ 1.70s(15), $\delta_{CH_2CH_3}$ 3.6q(4), 1.19 p.p.m. t(6).

[$(C_5Me_5)Ir(S_2CNEt_2)Cl$]. Prepared as above using $[(C_5Me_5)IrCl_2]_2$ (95 mg, 0.12 mmol) and $NaS_2CNEt_2.3H_2O$ (54 mg, 0.24 mmol). The bright orange product was recovered using pentane. Yield 100 mg, 82%.

[$(C_5Me_5)Rh(S_2CNEt_2)PEt_3$]$BPh_4$. $[(C_5Me_5)Rh(S_2CNEt_2)Cl]$ was stirred with a slight molar excess of PEt_3 in methanol for 5 minutes. Methanolic $NaBPh_4$ was added to precipitate the bright orange product. Yield 75%. Found, C 65.8, H 7.7, N 1.9; Calc. for $C_{45}H_{60}NS_2PBRh$, C 65.6, H 7.3, N 1.7. $^{31}P-\{^1H\}$ n.m.r. $CDCl_3$/298°K δP 30.5 p.p.m. $^1J_{RhP}$ 141.6Hz.

REACTION OF [$(C_5Me_5)Rh(S_2CNMe_2)Cl$] (106) WITH dppe.

$[(C_5Me_5)Rh(S_2CNMe_2)Cl]$ (63 mg, 0.16 mmol) dissolved in $CHCl_3$ (10 ml) was added dropwise over a 10 minute period to an ice-cooled, rapidly stirred $CHCl_3$ (20 ml) solution containing dppe (85 mg, 0.21 mmol). The resulting orange solution was reduced to 1/4 volume and methanolic (15 ml) $NaBPh_4$ (200 mg, 0.5 mmol) added to precipitate the orange binuclear complex *{[$(C_5Me_5)Rh(S_2CNMe_2)$]$_2$(μ-dppe)}[BPh_4]$_2$ (108)* Yield 86 mg. Found, C 67.6, H 5.92, N 1.55; Calc. for $C_{100}H_{106}N_2S_4P_2B_2Rh_2$, C 68.5, H 6.09, N 1.60. $^{31}P-\{^1H\}$ n.m.r. run in CH_2Cl_2/d^6-acetone/298°K, deceptively simple triplets as A portion of AA'XX' spectrum δP 34.9 p.p.m., $^3J_{PP}$ 15.9, $^1J_{RhP}$ 148.3, $^4J_{RhP}$ 0.6Hz. The filtrate was reduced to ½

volume and stored at 0°C for 24 hours to precipitate the orange dangling dppe complex [$(C_5Me_5)Rh(S_2CNMe_2)(dppe\text{-}P)$]-$BPh_4$ (107). Yield 28 mg, m.p. 153°C. [$(C_5Me_5)Rh(S_2CNEt_2)$-$(dppe\text{-}P)$]BPh_4 (109). [$(C_5Me_5)Rh(S_2CNEt_2)Cl$] (0.305 g, 0.72 mmol) dissolved in $CHCl_3$ (25 ml) was added dropwise over a 10 minute period to an ice-cooled, rapidly stirred $CHCl_3$ (40 ml) solution containing dppe (0.302, 0.76 mmol). The resulting orange solution was reduced to about 1/4 volume and methanolic (30 ml) $NaBPh_4$ (0.36 g, 1.05 mmol) was added to precipitate the orange product which was collected by filtration, washed with small amounts of cold MeOH and dried *in vacuo*. Yield 0.67 g, 85%, m.p. 176°C. Prepared using an analogous method were the complexes [$(C_5Me_5)Rh(S_2CNEt_2)$-$(dppm\text{-}P)$]BPh_4 (110). Orange solid prepared using [$(C_5Me_5)Rh(S_2CNEt_2)Cl$] (0.234 g, 0.56 mmol) and dppm (0.220, 0.57 mmol). Yield 0.55 g, 90%, m.p. 180°C. $^{13}C\text{-}\{^1H\}$ n.m.r. run in $CDCl_3$ at 298°K. $\delta_{C_5Me_5}$ 101.3, $^1J_{RhC}$ 5.1, $^2J_{PC}$ 2.4, 8.58; $\delta_{CH_2CH_3}$ 44.8, 12.06; δ_{CN} 206.2, $^2J_{RhC}$ 1Hz; $\delta_{C_5H_6}$ 120-140 p.p.m. The position of the methylene carbon of the dppm ligand was not established.

[$(C_5Me_5)Rh(S_2CNEt_2)(dppp\text{-}P)$]$BPh_4$ (111). Orange solid prepared using an equimolar quantity of [$(C_5Me_5)Rh(S_2CNEt_2)Cl$] and dppp. Yield 60%. [$(C_5Me_5)Rh(S_2CNEt_2)(dmpe\text{-}P)$]$BPh_4$ (112). Orange solid prepared using an approximate equimolar quantity of [$(C_5Me_5)Rh(S_2CNEt_2)Cl$] and dmpe. Yield 72%. [$(C_5Me_5)Ir(S_2CNEt_2)(dppm\text{-}P)$]$BPh_4$ (113). Bright yellow solid prepared using [$(C_5Me_5)Ir(S_2CNEt_2)Cl$] (36 mg, 0.07 mmol)

and dppm (28 mg, 0.072 mmol). Yield 58 mg, 70%, m.p. 176°C. $^{13}C-\{^1H\}$ n.m.r. run in $CDCl_3$ at 298°K. $\delta_{C_5Me_5}$ 95.9, $^2J_{PC}$ 2.6Hz, 8.23; $\delta_{CH_2CH_3}$ 44.25, 12.16; δ_{CN} 209.1; $\delta_{C_5H_6}$ 121-141 p.p.m. The position of the methylene carbon of the dppm ligand was not established.

REACTION OF $[(C_5Me_5)Ir(S_2CNEt_2)Cl]$ WITH dppe. A mixture of the dangling-$[(C_5Me_5)Ir(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ and bridging-dppe $\{[(C_5Me_5)Ir(S_2CNEt_2)]_2(\mu\text{-dppe})\}[BPh_4]_2$ (δP 0.8 p.p.m.) species were recovered from the equimolar reaction. Simple chemical methods could not separate the two species. The complexes $[(C_5Me_5)Rh(S_2PMe_2)(dppm\text{-}P)]Cl$ (115) (see text for $^{31}P-\{^1H\}$ n.m.r. parameters), $[(C_5Me_5)Rh(S_2PMe_2)(dppe\text{-}P)]Cl$ (116) δP_A 33.7, $^1J_{RhP}$ 146.3, $^3J_{P_AP_B}$ 31.7, $^3J_{P_AP_C}$ 12.2; δP_B -11.5 δ_{P_C} 100.1 p.p.m. $^2J_{RhP_C}$ 10.2Hz and $[(C_6H_6)Ru(S_2PPh_2)(dppe\text{-}P)]Cl$ (117) δP_A 31.6, $^3J_{P_AP_B}$ 34.2, $^3J_{P_AP_C}$ 17.1Hz; δP_B -12.1; δP_C 83.0 p.p.m. were prepared *in situ* in $CDCl_3$ at 298°K by the equimolar reaction of the appropriate metal-chloro complex and diphosphine.

The dangling diphosphine complexes are extremely soluble in chloroform, methylene chloride, acetone, nitromethane and in some cases diethyl ether and toluene solvent. They are insoluble in alcohols and linear hydrocarbon solvents.

The heterobimetallic complexes (118-130) were prepared using a standard procedure which is illustrated for the preparation of $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(p\text{-cym})]BPh_4$ (118). $[(p\text{-cym})RuCl_2]_2$ (34 mg, 0.056 mmol) was dissolved in

chloroform (15 ml). $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110) (124 mg, 0.12 mmol) dissolved in chloroform (10 ml) was added with stirring over a 5 minute period. The red solution was reduced to a small volume and methanol (15 ml) added to precipitate a light red microcrystalline solid. A small quantity of $NaBPh_4$ could be added to ensure high yield recovery of the product, which was filtered off, washed with small amounts of cold methanol and diethyl ether and dried *in vacuo*. Yield 140 mg, 84%. FAB mass spectrum +ve ion run in dmf/thioglycerol matrix, 1077 m/e corresponding to parent cation (118), 771 m/e corresponding to cation (110) accounted for by loss of $RuCl_2(p\text{-cym})$ fragment from parent. $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)RuCl_2(p\text{-}cym)]BPh_4$ (119). Prepared using $[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (109) (111 mg, 0.1 mmol) and $[(p\text{-cym})RuCl_2]_2$ (31 mg, 0.05 mmol). Yield 109 mg, 77%. $[(C_5Me_5Rh(S_2CNEt_2)(\mu\text{-}dppp)RuCl_2(p\text{-}cym)]BPh_4$ (120). Prepared using $[(C_5Me_5)Rh(S_2CNEt_2)(dppp\text{-}P)]BPh_4$ (111) (80 mg, 0.072 mmol) and $[(p\text{-cym})RuCl_2]_2$ (22 mg, 0.031 mmol). Yield 56 mg, 55%. $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dmpe)RuCl_2(p\text{-}cym)]\text{-}BPh_4$ (121). Prepared using $[(C_5Me_5)Rh(S_2CNEt_2)(dmpe\text{-}P)]BPh_4$ (112) (44 mg, 0.051 mmol) and $[(p\text{-cym})RuCl_2]_2$ (16 mg, 0.026 mmol). Yield 30 mg, 50%. $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)\text{-}RuCl_2(C_6H_6)]BPh_4$ (122). Prepared using (110) (150 mg, 0.14 mmol) and $[(C_6H_6)RuCl_2]_2$ (34.4 mg, 0.07 mmol). Yield 149 mg, 81%. $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6Me_6)]BPh_4$ (123). Prepared using (110) (65 mg, 0.06 mmol) and $[(C_6Me_6)RuCl_2]_2$ (20 mg, 0.03 mmol). Yield 59 mg, 69%. FAB mass spectrum +ve ion run in dmf/thioglycerol matrix, 1106 m/e corresponding

to parent cation (123), 771 m/e corresponding to cation (110) accounted for by loss of $RuCl_2(C_6Me_6)$ fragment from parent. [$(C_5Me_5)Rh(S_2CNEt_2)(\mu$-dppm)$OsCl_2$(p-cym)]$BPh_4$ (124) Prepared using (110) (95 mg, 0.087 mmol) and $[(p\text{-cym})OsCl_2]_2$ (34 mg, 0.038 mmol). Yield 110 mg, 85%. [$(C_5Me_5)Ir(S_2CNEt_2)(\mu$-dppm)$RuCl_2$(p-cym)]$BPh_4$ (125). Prepared using $[(C_5Me_5)Ir(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (113) (31 mg, 0.026 mmol) and $[(p\text{-cym})RuCl_2]_2$ (8 mg, 0.013 mmol). Yield 28 mg, 72%. [$(C_5Me_5)Ir(S_2CNEt_2)(\mu$-dppm)$RuCl_2(C_6Me_6)]BPh_4$ (126). Prepared using (113) (32 mg, 0.027 mmol) and $[(C_6Me_6)RuCl_2]_2$ (9 mg, 0.013 mg). Yield 30 mg, 73%. [$(C_5Me_5)Rh(S_2CNMe_2)(\mu$-dppe)$RuCl_2$(p-cym)]$BPh_4$ (127). Prepared using $[(C_5Me_5)Rh(S_2CNMe_2)(dppe\text{-}P)]BPh_4$ (107) (27 mg, 0.025 mmol) and $[(p\text{-cym})RuCl_2]_2$ (8 mg, 0.013 mmol). Yield 24 mg, 69%. [$(C_5Me_5)Rh(S_2CNEt_2)(\mu$-dppe)$RuCl_2(C_6Me_6)]BPh_4$ (127). Prepared using (109) (70 mg, 0.063 mmol) and $[(C_6Me_6)RuCl_2]_2$ (21 mg, 0.032 mmol). Yield 62 mg, 68%. [$(C_5Me_5)Rh(S_2CNEt_2)(\mu$-dppe)$OsCl_2$(p-cym)]$BPh_4$ (129). Prepared using (109) (47 mg, 0.043 mmol) and $[(p\text{-cym})OsCl_2]_2$ (17 mg, 0.022 mmol). Yield 51 mg, 80%. [$(C_5Me_5)Rh(S_2CNEt_2)$-$(\mu$-dppe)$RhI_2(C_5Me_5)]BPh_4$ (130). Prepared *in situ* using a respective 2:1 molar ratio of (109) and $[(C_5Me_5)RhI_2]_2$. [$(C_5Me_5)Rh(S_2CNEt_2)(\mu$-dppm)IrCl(COD)]$BPh_4$ (131). Prepared by mixing (110) (55 mg, 0.05 mmol) and $[CODIrCl]_2$ (17 mg, 0.025 mmol) in $CDCl_3$ at 298°K and characterised *in situ* by $^{13}P\text{-}\{^1H\}$ n.m.r. (see Table 13) and ^1H n.m.r. spectroscopy, ^1H n.m.r. data $\delta_{C_5Me_5}$ 1.29d(15), $^4J_{PH}$ 3.2Hz; $\delta_{CH_2CH_3}$ 1.28t(6), 3.51(4) centre ABM_3 pattern; δ_{COD} alkene 5.0br(2) H *trans* to P,

2.27 br(2) H trans to Cl, aliphatic 1.4-2.2 br; δ_{CH_2} dppm 4.27't'(2); $\delta_{C_6H_5}$ 6.8-7.5 p.p.m.

[$(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})IrCl(COD)]BPh_4$ (132). Prepared using (109) (62 mg, 0.056 mmol) and $[CODIrCl]_2$ (19 mg, 0.028 mmol) and characterised in situ.

[$(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RuCl(PPhMe_2)(p\text{-cym})][BPh_4]_2$ (133). Prepared by stirring $[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(p\text{-cym})]$-$BPh_4$ (118) with a slight molar excess of $PPhMe_2$ in a chloroform/methanol mixed solvent (2:3 vol/vol) in the presence of one equivalent of $NaBPh_4$ at room temperature for 24 hours. Obtained as the minor component (∿30%) in a mixture with (118) and characterised by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. $^{31}P-\{^1H\}$ n.m.r. data ($CDCl_3$/298°K), δP_{RhP} 34.7dd, $^1J_{PRh}$ 145.1, $^2J_{PP}$ 51.8; δP_{RuP} (dppm) 26.0ddd, $^3J_{RhP}$ 4.2; δP_{RuP} ($PPhMe_2$) 5.1 p.p.m. d , $^2J_{PP}$ 55.1Hz.

[$(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})Ru(p\text{-cym})(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]$-$[BPh_4]_2$ (134). The compound $[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]$-$BPh_4$ (109) (46 mg, 0.042 mmol) was mixed with $[(p\text{-cym})RuCl(\mu\text{-}SPPh_2)_2Pt(S_2CN^iPr_2)]$ (74) (45 mg, 0.042 mmol) in chloroform (4 ml) to give an immediate reaction. A methanol solution (20 ml) containing 1.5 equivalents of $NaBPh_4$ was added to precipitate the light red product. Yield 91 mg, 88%. Found C 63.9, H 5.7, N 1.4; Calc. for $C_{130}H_{137}N_2P_2S_6B_2RhRuPt$, C 63.4, H 5.6, N 1.1; i.r., KBr disc spectrum, ν_{CN} 1510; ν_{PS} 576 cm^{-1}. $^{31}P-\{^1H\}$ n.m.r. data, see text. ^1H n.m.r. data $CDCl_3$/303°K. $\delta_{C_5Me_5}$ 1.22d, $^4J_{PH}$ 3.2Hz; $\delta_{CH_2CH_3}$ 0.8t, 3.18 centre ABM_3; $\delta_{CH(CH_3)_2}$

(dithiocarbamate) 0.80d, 4.25br; p-cymene ring:

δ_{CH_3} 1.53s, $\delta_{CH(CH_3)_2}$ 0.40d, 2.3br; $\delta_{C_6H_4}$ 5.1br;
δ_{CH_2} (dppe) 2.44br, 1.42br; $\delta_{C_6H_5}$ 6.8-7.6 p.p.m.

TABLE 12: MICROANALYTICAL, INFRA-RED AND CONDUCTIVITY DATA (CH_3NO_2) FOR COMPLEXES PREPARED IN CHAPTER 4

COMPLEX	% FOUND			% CALCULATED				SLOPE OF
	C	H	N	C	H	N	i.r.data/cm^{-1}	$\Lambda_\infty - \Lambda_e$ vrs $Ce^{\frac{1}{2}}$
$[(C_5Me_5)Rh(S_2CNMe_2)(dppe\text{-}P)]BPh_4$ (107)	70.2	6.0	1.3	70.3	6.1	1.3	1542	
$[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (109)	71.1	6.3	1.6	70.7	6.3	1.3	1517	303
$[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110)	70.6	6.3	1.4	70.5	6.2	1.3	1514	336
$[(C_5Me_5)Rh(S_2CNEt_2)(dppp\text{-}P)]BPh_4$ (111)	70.9	6.4	1.6	70.9	6.4	1.3	1512	
$[(C_5Me_5)Ir(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (113)	65.9	5.8	1.5	65.2	5.7	1.2	1520	352
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(p\text{-}cym)]BPh_4$ (118)	63.3	5.8	1.2	63.7	5.8	1.0	1512,288,278	296
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)RuCl_2(p\text{-}cym)]BPh_4$ (119)	62.7	5.7	1.0	63.4	5.8	1.0	1506,288,278	
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6H_6)]BPh_4$ (122)	61.8	5.4	1.1	62.7	5.5	1.0	1514,290,274	
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)OsCl_2(p\text{-}cym)]BPh_4$ (124)	59.2	5.5	1.2	59.8	5.5	1.0	-	
$[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(p\text{-}cym)]BPh_4$ (125)	59.1	5.5	1.2	59.8	5.5	0.9	1515,290,278	
$[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6Me_6)]BPh_4$ (126)	58.1	5.3	1.1	60.3	5.6	0.9	1522,295,287	
$[(C_5Me_5)Rh(S_2CNMe_2)(\mu\text{-}dppe)RuCl_2(p\text{-}cym)]BPh_4$ (127)	62.7	5.7	1.0	63.4	5.8	1.0	1541	
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)RuCl_2(C_6Me_6)]BPh_4$ (128)	63.9	6.1	1.2	64.3	6.1	1.0	-	

TABLE 13: PHOSPHORUS-31-{^{1}H} NMR DATA FOR COMPLEXES PREPARED IN CHAPTER 4 $CDCl_3$/298°K

COMPLEX	δP_A/ppm	$^1J_{RhP_A}$/Hz	δP/ppm	J_{PP}/Hz	J_{RhP}/Hz	SPECTRAL TYPE
$[(C_5Me_5)Rh(S_2CNMe_2)(dppe\text{-}P)]BPh_4$ (107)	32.9	145.9	-11.9	33.0	n/m	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (109)	34.1	145.9	-12.3	34.2	0.4	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110)	32.2	146.5	-26.8	35.4	3.7	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(dppp\text{-}P)]BPh_4$ (111)	30.4	146.0	-19.0	2.0	n/m	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(dmpe\text{-}P)]BPh_4$ (112)	11.6	144.0	-44.7	29.2	n/m	AMX
$[(C_5Me_5)Ir(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (113)	-1.9		-27.9	40.3		AX
$[(C_5Me_5)Ir(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (114)	0.2		-12.5	35.9		AX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(p\text{-}cym)]BPh_4$ (118)	29.9	144.4	23.0	52.3	4.4	ABX→AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)RuCl_2(p\text{-}cym)]BPh_4$ (119)	32.3	144.0	23.9	25.9	n/m	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppp)RuCl_2(p\text{-}cym)]BPh_4$ (120)	30.1	145.3	23.8	1.0	n/m	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dmpe)RuCl_2(p\text{-}cym)]BPh_4$ (121)	11.3	132.8	8.4	28.4	11.3	ABX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6H_6)]BPh_4$ (122)	30.1	144.5	23.9	52.7	4.7	ABX→AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6Me_6)]BPh_4$ (123)	29.6	142.8	28.8	50.1	3.9	ABX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)OsCl_2(p\text{-}cym)]BPh_4$ (124)	27.0	145.3	-20.5	51.3	3.6	AMX

TABLE 13 (continued)

	δP_A/ppm	J_{RhP_A}/Hz	δP/ppm	J_{PP}/Hz	J_{RhP}/Hz	SPECTRAL TYPE
$[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(p\text{-cym})]BPh_4$ (125)	-5.4		21.0	52.1		AX
$[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(C_6Me_6)]BPh_4$ (126)	-5.3		27.4	50.3		AX
$[(C_5Me_5)Rh(S_2CNMe_2)(\mu\text{-dppe})RuCl_2(p\text{-cym})]BPh_4$ (127)	33.8	144.0	24.2	24.4	1.5	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})RuCl_2(C_6Me_6)]BPh_4$ (128)	34.6	144.1	28.9	25.1	1.7	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})OsCl_2(p\text{-cym})]BPh_4$ (129)	33.3	144.0	-16.6	26.9	n/m	AMX
$[(C_5Me_5)Rh(S_2CNMe_2)(\mu\text{-dppe})RhI_2(C_5Me_5)]BPh_4$ (130)	34.0	145.3	27.1	23.2	152.0	ABXY
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppm})IrClCOD]BPh_4$ (131)	30.0	145.5	13.6	38.0	3.9	AMX
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-dppe})IrClCOD]BPh_4$ (132)	34.9	145.3	15.4	25.6	n/m	AMX

TABLE 14: HYDROGEN-1 NMR DATA[a] FOR COMPLEXES PREPARED IN CHAPTER 4 $CDCl_3$/298°K

COMPLEX	δC_5Me_5[b]	$S_2CNR_2^-$ δCH_2	$S_2CNR_2^-$ δCH_3	P P δCH_2	δarene	δC_6H_5[r]
$[(C_5Me_5)Rh(S_2CNMe_2)(dppe\text{-}P)]BPh_4$ (107)	1.33(3.2)	-	2.78	1.80,2.40[i]		6.8-7.5
$[(C_5Me_5)Rh(S_2CNEt_2)(dppe\text{-}P)]BPh_4$ (109)	1.32(3.3)[c]	3.39[g]	1.06[h]	1.84,2.44[i]		7.0-7.6
$[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (110)	1.34(3.3)	3.41[f]	1.00[h]	3.10[j]		7.0-7.5
$[(C_5Me_5)Ir(S_2CNEt_2)(dppm\text{-}P)]BPh_4$ (113)	1.39(2.2)	3.24[f]	0.99[h]	3.27[j]		7.0-7.5
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(p\text{-}cym)]BPh_4$ (118)	1.27(3.2)	3.55[d e]	1.11[h]	4.18[j]	0.85[ℓ] 1.58[m] 2.23[n] 4.98[o,p]	6.8-7.5
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)RuCl_2(p\text{-}cym)]BPh_4$ (119)	1.32(3.1)	3.27[f]	0.92[h]	1.51,2.44[i]	0.90[ℓ] 1.83[m] 2.47[n] 5.06[o]	6.8-7.6
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6H_6)]BPh_4$ (122)	1.29(3.2)	3.48[e]	1.06[h]	4.13[j]	5.08(0.87)[q]	6.8-7.5
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6Me_6)]BPh_4$ (123)	1.36(2.9)	3.23[g]	0.90[h]	4.16[k]	1.61(n/m)[q]	6.8-7.6
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppm)OsCl_2(p\text{-}cym)]BPh_4$ (124)	1.27(3.1)	3.70[e]	1.13[h]	4.42[j]	0.87[ℓ] 1.69[m] 2.00[n] 5.20[o]	6.8-7.4
$[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(p\text{-}cym)]BPh_4$ (125)	1.32(2.1)	3.43[e]	1.12[h]	4.31[j]	0.83[ℓ] 1.59[m] 2.22[n] 4.98[o,p]	6.8-7.5
$[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-}dppm)RuCl_2(C_6Me_6)]BPh_4$ (126)	1.40(2.1)	3.11[g]	0.91[h]	4.25[k]	1.61(0.8)[q]	6.9-7.4
$[(C_5Me_5)Rh(S_2CNMe_2)(\mu\text{-}dppe)RuCl_2(p\text{-}cym)]BPh_4$ (127)	1.34(3.2)	-	2.80	1.53,2.44[i]	0.94[ℓ] 1.81[m] 2.49[n] 5.06[o]	6.8-7.6
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)RuCl_2(C_6Me_6)]BPh_4$ (128)	1.32(3.0)	3.30[f]	0.97[h]	1.48,2.42[i]	1.66(n/m)[q]	6.8-7.6
$[(C_5Me_5)Rh(S_2CNEt_2)(\mu\text{-}dppe)OsCl_2(p\text{-}cym)]BPh_4$ (129)	1.32(3.1)	3.32[f]	0.95[h]	1.51,2.56[i]	0.98[ℓ] 1.93[m] 2.32[n] 5.24[o]	6.8-7.6

NOTES FOR TABLE 14

a δ_H/ppm; J_{XY}/Hz

b $^4J_{PH}$ values in parentheses

c $^3J_{RhH}$ value of 0.3Hz obtained on line narrowing C_5Me_5 resonance

d Irradiation of δ_{CH_3} 1.11 p.p.m. triplet caused δ_{CH_2} 3.55 p.p.m. ABM_3 pattern to collapse to an AB pattern.

e Value given is centre of ABM_3 pattern. 'Large' difference in δ_{AB} (see Figure 22).

f Value given is centre of ABM_3 pattern. 'small' difference in δ_{AB}

g Overlapping quartet pattern

h Triplet resonances $^3J_{HH}$ 7.2Hz

i Broad multiplets for δ_{CH_2} groups of dppe ligand

j 'Doublet of doublet' pattern

k 'Triplet' pattern

ℓ $\delta_{CH(C\underline{H}_3)}$ doublet resonance $^3J_{HH}$ 6.9Hz

m δ_{CH_3} singlet resonance

n $\delta_{C\underline{H}(Me)_2}$ septet resonance

o Arene proton resonance AB pattern (118) J_{HH} 6.3, $\Delta\nu$9.2; (119) 5.2, 30.4; (124) A_2 spectrum; (125) 6.2, 11.4; (127) 5.2, 21.8; (129) 5.4Hz, 12.2Hz

p Small splitting observed on high-frequency portion of AB pattern

q Singlet resonances J_{PH} values in parentheses

r Broad overlapping multiplet resonances for phenyl groups of diphosphine ligand and BPh_4^- counteranion.

TABLE 15: Selected Bond Distances and Angles for the Cation $[(C_5Me_5)Rh(S_2CNEt_2)(dppm\text{-}P)]^+$ (110) with Estimated Standard Deviations in Parentheses

a) Distances (Å)

Rh(1) - P(1)	2.3148(19)	C(1) - P(2)	1.861(8)
Rh(1) - S(1)	2.3687(20)	S(1) - C(2)	1.730(8)
Rh(1) - S(2)	2.3734(21)	S(2) - C(2)	1.723(8)
P(1) - C(1)	1.838(8)	C(2) - N(1)	1.310(10)
Rh(1) - C(C_5Me_5)	2.201(8)-2.232(8)		

b) Angles (degrees)

P(1) - Rh(1) - S(1)	89.24(7)	P(1) - C(1) - P(2)	115.2(4)
P(1) - Rh(1) - S(2)	92.76(7)	Rh(1) - S(1) - C(2)	88.3(3)
S(1) - Rh(1) - S(2)	73.29(7)	Rh(1) - S(2) - C(2)	88.3(3)
Rh(1) - P(1) - C(1)	114.7(3)	S(1) - C(2) - S(2)	110.1(4)

TABLE 16: Selected Bond Distances and Angles for the Cation $[(C_5Me_5)Ir(S_2CNEt_2)(\mu\text{-dppm})RuCl_2(C_6Me_6)]^+$ (126) with Estimated Standard Deviations in Parentheses

a) Distances (Å)

Ir(1) - S(1)	2.376(6)	Ir(1) - P(2)	2.300(5)
Ir(1) - S(2)	2.380(6)	P(2) - C(1)	1.829(16)
S(1) - C(2)	1.653(24)	C(1) - P(1)	1.861(16)
S(2) - C(2)	1.732(24)	Ru(1) - P(1)	2.359(5)
C(2) - N(1)	1.40(3)	Ru(1) - Cl(1)	2.407(5)
		Ru(1) - Cl(2)	2.417(5)

Ir(1) - $C(C_5Me_5)$	2.196(13) - 2.217(13)
Ru(1) - $C(C_6Me_6)$	2.208(11) - 2.245(11)

b) Angles (degrees)

P(2) - Ir(1) - S(1)	90.71(19)	C(1) - P(1) - Ru(1)	110.6(5)
P(2) - Ir(1) - S(2)	91.77(18)	P(1) - Ru(1) - Cl(1)	87.84(16)
S(1) - Ir(1) - S(2)	73.02(21)	P(1) - Ru(1) - Cl(2)	85.68(17)
Ir(1) - P(2) - C(1)	110.2(5)	Cl(1) - Ru(1) - Cl(1)	86.63(17)
P(1) - C(1) - P(2)	133.1(9)		

CHAPTER 5

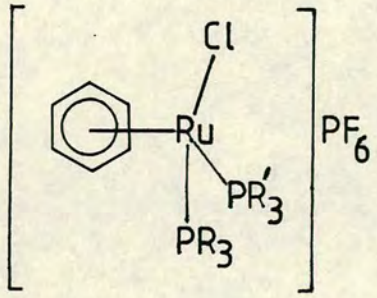
THE SYNTHESIS OF MONONUCLEAR RUTHENIUM(II) COMPLEXES CONTAINING DANGLING DIPHOSPHINE LIGANDS AND THEIR USE IN THE SYNTHESIS OF HOMO- AND HETERO-BIMETALLIC COMPLEXES

5.1 INTRODUCTION

Preliminary investigation into the chemistry of the heterobimetallics $[(C_5Me_5)M(III)(S_2CNEt_2)(\mu\text{-diphosphine})\text{-}M(II)Cl_2(arene)]BPh_4$ (118-129), produced in Chapter 4, indicated that reactivity was restricted to substitution of a terminal chloride ligand on the M(II) ion. As a next step it was decided to develop systems in which each metal had the potential, through suitable reactive sites, to participate in further reaction.

5.2 SYNTHESIS OF MONONUCLEAR COMPLEXES CONTAINING DANGLING DIPHOSPHINE AND TERMINAL CHLORIDE LIGANDS

Recently mononuclear ruthenium complexes of the type $[(C_6H_6)RuCl(PR_3)(PR'_3)]PF_6$ (135) have been prepared by treating $[(C_6H_6)RuCl_2PR_3]$ with PR'_3 in methanol in the presence of NH_4PF_6.[149]



(135)

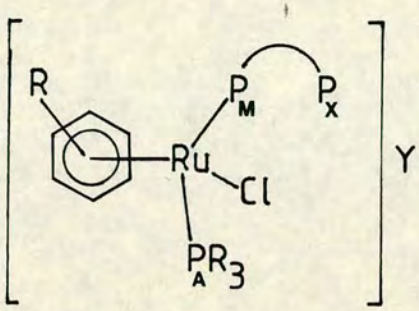
		$^{31}P\text{-}\{^1H\}$ nmr data/$CDCl_3$		
PR_3	PMe_3	δPR_3	$\delta PR'_3$	$^2J_{PP}$
PMe_2Ph	PMe_3	7.23	3.15	61.0
PPh_3	PMe_3	18.28	-1.14	56.6
$P(OMe)_3$	PMe_3	123.81	9.78	91.6
PPh_3	PMe_2Ph	28.83	2.71	55.9
PPh_3	$PMePh_2$	24.89	13.16	55.1

An investigation into the reaction of $[(arene)RuCl_2PR_3]$ with the diphosphines dppm, dppe and dppp was undertaken with

the aim of producing monocationic products of the type [(arene)RuCl(PR_3)(diphosphine-P)]Y. These complexes could then be used as precursors in the synthesis of bi-metallics by coordinating a second metal fragment through the dangling phosphine while retaining a terminal chloride ligand, shown for the complexes (135) to be a site capable of further reaction (Chapter 3, Scheme 9).

An equimolar quantity of the monophosphine complex [(arene)$RuCl_2PR_3$] (arene = C_6H_6, p-cymene; PR_3 = PPh_3, $PPhEt_2$, $PPhMe_2$, $P(OMe)_3$) and diphosphine (dppm, dppe, dppp) were dissolved in CH_2Cl_2. A slight molar excess of either $NaBPh_4$ or NH_4PF_6 in methanol was then added to give a CH_2Cl_2 : MeOH ratio by volume of 1:5. The red reaction solution was stirred at room temperature under dinitrogen and after three hours a yellow solid began to precipitate from the solution. After 16 hours stirring, the yellow product was filtered off and washed with cold methanol. A second batch of product was recovered on reducing the volume of the light-red filtrate. No reaction was observed in the absence of $NaBPh_4$ or NH_4PF_6, with reactions involving the former requiring less time to proceed to completion. The products have been characterised on the basis of ^1H, $^{31}P-\{^1H\}$ n.m.r. and i.r. spectroscopy and microanalytical data as the monocationic complexes [(arene)Ru(PR_3)(diphosphine-P)Cl]Y (136-145). The products are air-stable, yellow/green solids, which readily dissolve in chlorinated hydrocarbons and acetone. They are slightly soluble in alcohols and insoluble in ethers and hydrocarbons.

The $^{31}P-\{^{1}H\}$ n.m.r. spectra for the complexes [(arene)Ru(PR_3)(diphosphine-P)Cl] (136-145) show separate resonances for the tertiary phosphine ligand P_A and the coordinated P_M and dangling P_X phosphine atoms of the diphosphine ligand.

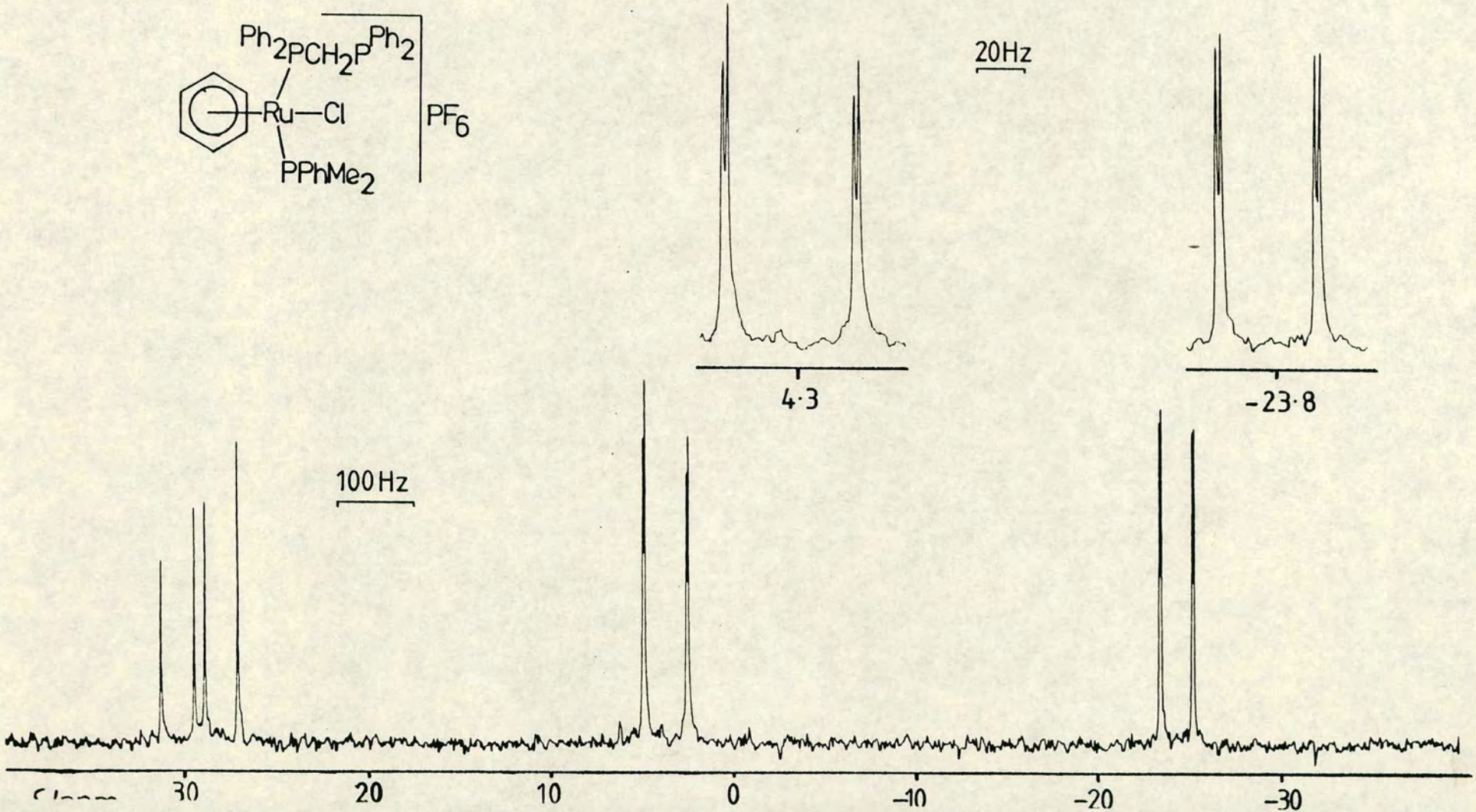


(136-145)

[(C_6H_6)Ru($PPhEt_2$)(dppe-P)Cl]PF_6 (136)
[(p-cym)Ru($PPhEt_2$)(dppe-P)Cl]BPh_4 (137)
[(C_6H_6)Ru($PPhMe_2$)(dppe-P)Cl]PF_6 (138)
[(p-cym)Ru($PPhMe_2$)(dppe-P)Cl]PF_6 (139)
[(C_6H_6)Ru(PPh_3)(dppe-P)Cl]BPh_4 (140)
[(p-cym)Ru($P(OMe)_3$)(dppe-P)Cl]BPh_4 (141)
[(C_6H_6)Ru($PPhMe_2$)(dppm-P)Cl]PF_6 (142)
[(p-cym)Ru($PPhMe_2$)(dppm-P)Cl]BPh_4 (143)
[(p-cym)Ru($P(OMe)_3$)(dppm-P)Cl]BPh_4 (144)
[(C_6H_6)Ru($PPhMe_2$)(dppp-P)Cl]PF_6 (145)

The spectrum of [(C_6H_6)Ru($PPhMe_2$)(dppm-P)Cl]$^+$ (142) [Figure 26] consists of 12 lines of approximately equal intensity arranged as three doublet of doublets and can be characterised by three chemical shifts (δP_A 4.3, δP_M 29.5, δP_X -23.8 p.p.m.) and three coupling constants ($^2J_{P_AP_M}$ 58.1, $^2J_{P_MP_X}$ 43.5, $^4J_{P_AP_X}$ 2.0Hz). Similarly under high resolution, the spectrum of [(C_6H_6)Ru($PPhEt_2$)-(dppe-P)Cl]$^+$ (136) [Figure 27] consists of 12 lines (only 8 visible in Figure 27) with two resonances between 20 and 30 p.p.m. for P_A (δP 22.6 p.p.m., $^2J_{P_AP_M}$ 55.0Hz) and P_M (δP 29.3 p.p.m., $^3J_{P_MP_X}$ 31.5Hz) bound at Ru with at lower frequency, the resonance for the dangling P_X atom (δP -12.3 p.p.m., $^5J_{P_AP_X}$

Figure 26 The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $[(C_6H_6)Ru(PPhMe_2)(dppm-P)Cl]PF_6$ (142) in $CDCl_3$ at 298°K



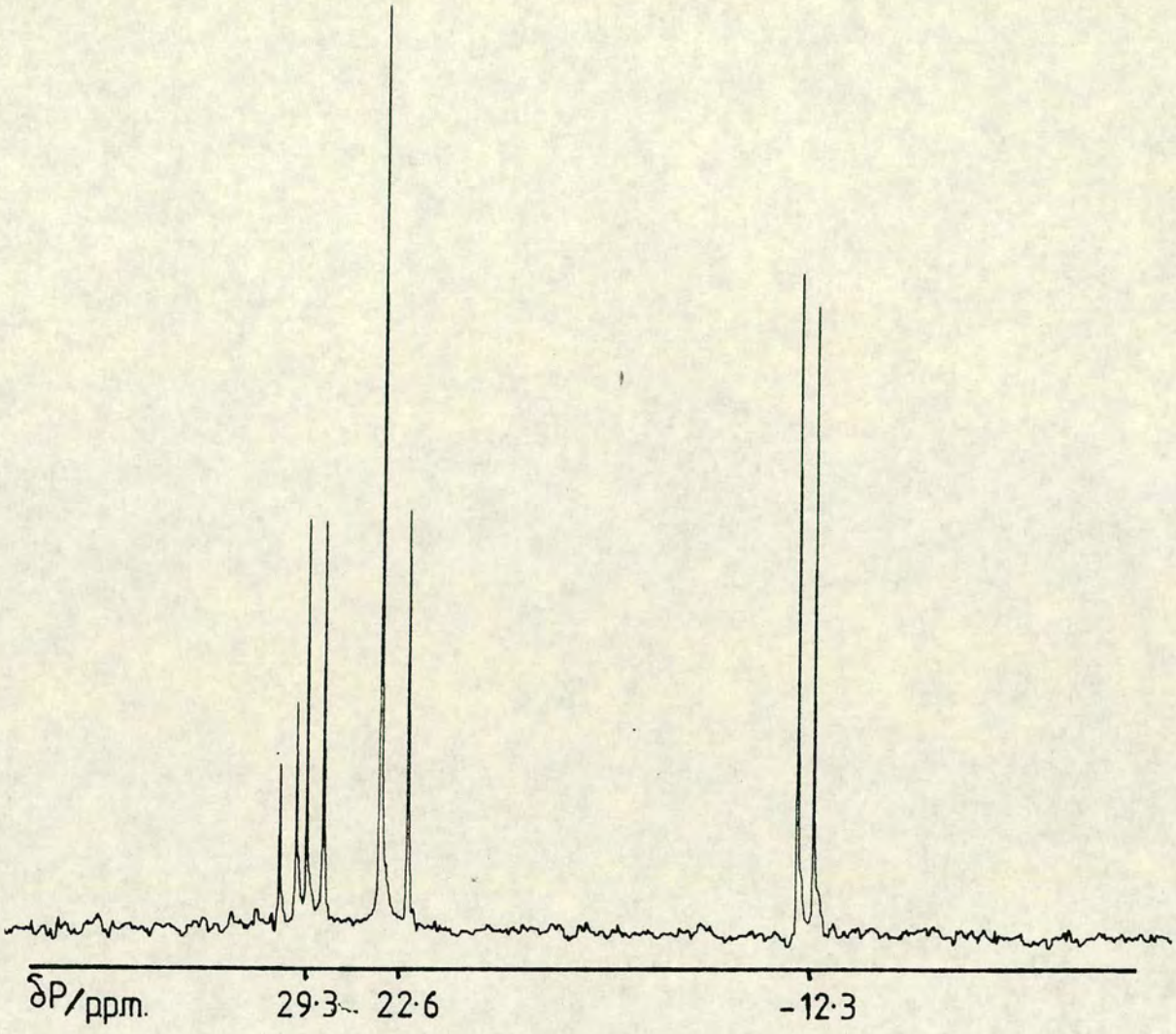


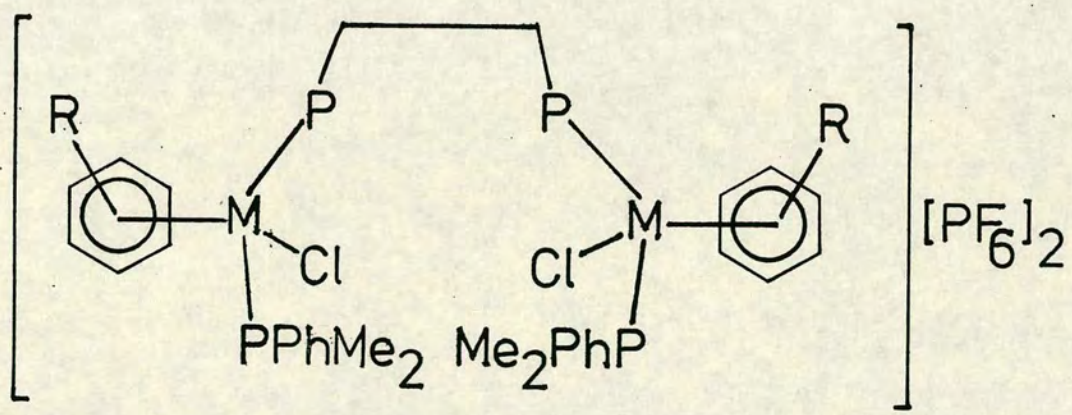
Figure 27: The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $[(C_6H_6)Ru(PPhEt_2)-(dppe-P)Cl]PF_6$ (136) in $CDCl_3$ at 298°K

1.0Hz). The difference in the intensities of the signals for the Ru bound P atoms in the spectrum of (136) is a result of the chemical shift difference between P_A and P_M approaching the size of the coupling constant between the atoms. This causes the spectrum to become more second order and lean toward an ABX pattern. An ABX pattern was observed for the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $[(C_6H_6)Ru(PPh_3)(dppe-P)Cl]-BPh_4$ (140). The ^{1}H n.m.r. spectra for the complexes (137), (140) and (142) reveal signals in the region 5.0-5.5 p.p.m., which confirm that the arene ring remains coordinated to Ru.

Also, in the i.r. spectra of several of the complexes (136-145) a weak band is found between 300-308 cm^{-1} for the terminal ν_{RuCl} stretching vibration.

5.3 SYNTHESIS OF DIPHOSPHINE BRIDGED HOMOBIMETALLICS

Treatment of the monophosphine complexes [(arene)MCl_2-($PPhMe_2$)] (M = Ru, arene = C_6H_6, p-cymene; M = Os, arene = p-cymene) with 0.5 equivalents of dppe in CH_2Cl_2/MeOH in the presence of NH_4PF_6 yields yellow products, which on evidence gathered from ^1H, $^{31}P-\{^1H\}$ n.m.r. spectroscopy, solution conductivity and microanalysis are formulated as the dppe-bridged homobimetallics {[(arene)$MCl(PPhMe_2)]_2$-(μ-dppe)}$[PF_6]_2$ (146-148).



(146-148)

{[(C_6H_6)RuCl($PPhMe_2$)]$_2$(μ-dppe)}$[PF_6]_2$ (146) [(p-cym)RuCl($PPhMe_2$)]$_2$-(μ-dppe)}$[PF_6]_2$ (147) {[(p-cym)OsCl($PPhMe_2$)]$_2$(μ-dppe)}$[PF_6]_2$ (148)

The products are insoluble in all common n.m.r. solvents except CD_3NO_2. The $^{31}P-\{^1H\}$ n.m.r. spectra for the complexes (146-148) are second order and consist of two sets of two pseudo triplets which can be analysed as derived from an AA'BB' spin system (see Figure 28 for the spectrum of $\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppe})\}^{2+}$ (146); δP_A ($PPhMe_2$) 5.8, δP_B (dppe) 30.9 p.p.m., $^3J_{P_BP_B'}$ 19.6, $^2J_{P_AP_B}$ ($^2J_{P_AP_B'}$) 59.2, $^5J_{P_AP_B'}$ ($^5J_{P_AP_B}$) 0.6Hz). The structure of (146) was confirmed by a single crystal X-ray diffraction study on crystals grown from a CD_3NO_2/MeOH mixture. The cation [Figure 29] has crystallographic Ci symmetry. A single-dppe ligand links the two Ru centres with an Ru.....Ru separation of 8.501(1)Å. The coordination sphere of each Ru centre is completed by a η^6-C_6H_6 arene ring, a terminal Cl ligand and the P donor atom of a dimethylphenyl-phosphine ligand. The P(1), P(2) and Cl atoms almost eclipse the carbon atoms C(2), C(4) and C(6) respectively of the benzene ring as shown by the torsion angles C(2)-X-Ru-P(1) of 3.9(3)°, C(4)-X-Ru-P(2) of -2.1(3)° and C(6)-X-Ru-Cl of 2.3(3)° where X is the ring centroid. The Ru-Cl (2.3980(25)Å) and Ru-P (2.3506(21), 2.341(3)Å) bond distances are comparable with the corresponding values found for similar systems.[215] The C_6H_6 ring is planar but the Ru-C bond distances vary significantly from Ru-C(3) of 2.224(6) to Ru-C(6) of 2.271(6)Å which suggests that the C_6H_6 ring is tilted toward Ru at C(3) and away from Ru at C(6) [see Figure 30]. The P(1)-Ru-P(2) bond angle of 92.27(8)° is greater than either the P(1)-Ru-Cl angle of 88.38(8)° or the P(2)-Ru-Cl angle

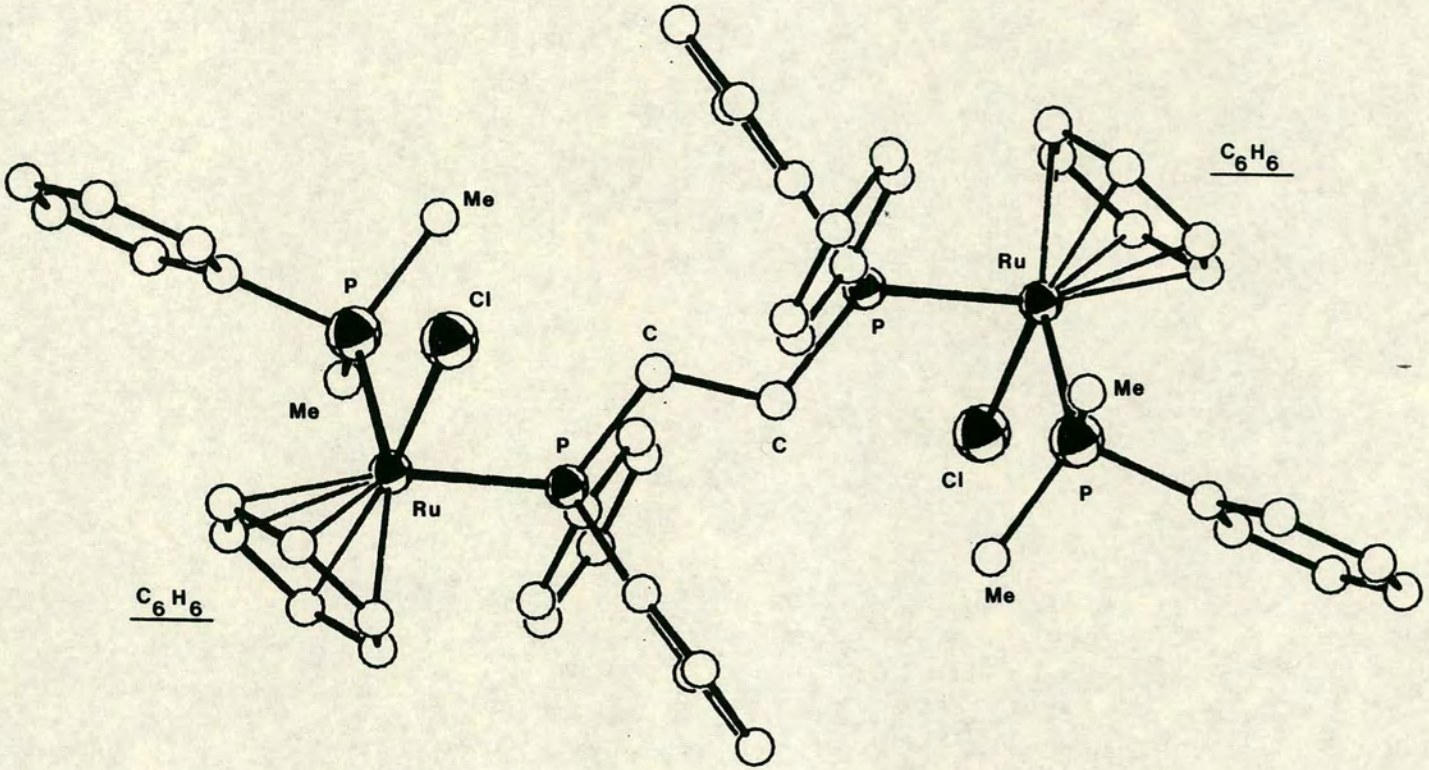
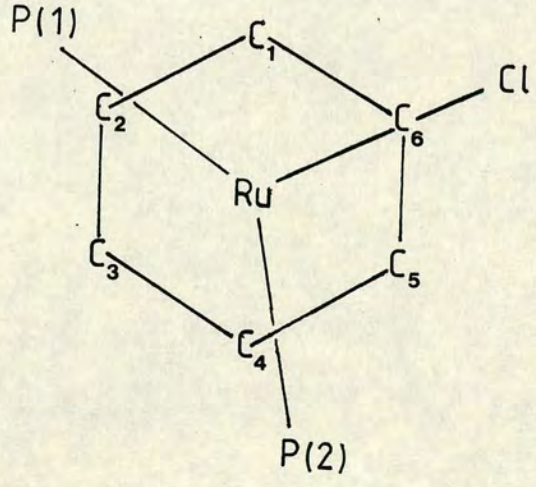


Figure 29 The molecular structure of the dication $\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppe})\}^{2+}$ (146)

of 88.76(9)° and it is this larger 'gap' into which the C(3) atom tilts. The differences in the Ru-C distances appear to be related to the trans-influence of the donor atoms P and Cl. For example, the shortest Ru-C distance of 2.224(6)Å is found for C(3) which is 'trans' to Cl. However, steric factors, such as the P(1)-P(2) 'gap', may also contribute to the differences in the Ru-C distances.

The reaction of $[(C_6H_6)RuCl_2PPhMe_2]$ with 0.5 equivalents of dppp in CH_2Cl_2/MeOH in the presence of NH_4PF_6 produced the dppp-bridged homobimetallic $\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppp})\}[PF_6]_2$ (149). However, attempts to produce the related dppm-bridged complex using similar conditions were unsuccessful and this may be due to the unfavourable steric requirements for such a product.[43]



Bond distances (Å)

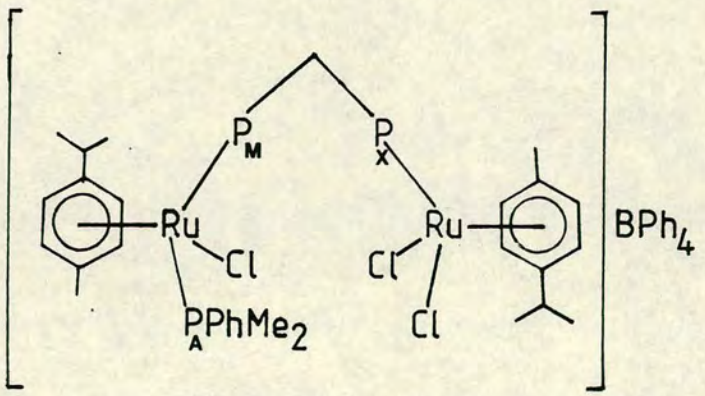
Ru-C(6)	2.271(6)
Ru-C(1)	2.261(6)
Ru-C(5)	2.256(6)
Ru-C(2)	2.238(6)
Ru-C(4)	2.233(6)
Ru-C(3)	2.224(6)

Figure 30: Diagram of the "$[(C_6H_6)RuP(1)P(2)Cl]$" fragment in the dication $\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppe})\}^{2+}$ (146)

5.4 THE SYNTHESIS OF HOMO- AND HETERO-BIMETALLIC COMPLEXES

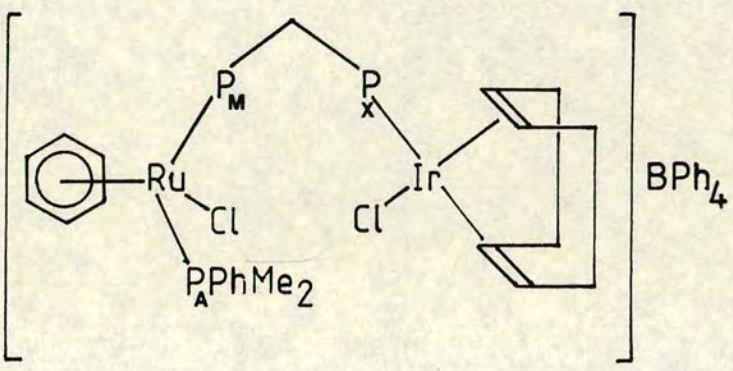
In Section 5.2 a number of ruthenium complexes of the type [(arene)Ru(PR_3)(diphosphine-P)Cl]Y (136-145) were prepared which contained both a dangling-diphosphine and a terminal-chloride ligand. It was the intention to use such complexes as precursors in the synthesis of bimetallic complexes which maintain sites on both metals to engage in further reaction. The versatile dichloro-bridged complexes $[(p\text{-cym})MCl_2]_2$ ((69) M = Ru, (70) M = Os) and $[CODIrCl]_2$ (35) were identified as likely to undergo bridge-cleavage reactions with the uncoordinated P atom in the 'metallo-ligands' (136-145).

The reaction of $[(p\text{-cym})RuCl_2]_2$ with two equivalents of $[(p\text{-cym})Ru(PPhMe_2)(dppm\text{-}P)Cl]BPh_4$ (143) in $CDCl_3$ at room temperature proceeds rapidly to give a product identified by $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy as the dppm-bridged heterobimetallic complex $[(p\text{-cym})Ru(PPhMe_2)Cl(\mu\text{-dppm})RuCl_2(p\text{-cym})]BPh_4$ (150). The product can be recovered as an air-



(150)

(151)



stablered solid on addition of methanol to the reaction solution.

The high resolution $^{31}P-\{^{1}H\}$ n.m.r. spectrum for (150) run in CD_2Cl_2 at 298°K shows three P resonances; a doublet for the monophosphine ligand (δP_A 4.0 p.p.m., $^{2}J_{P_AP_M}$ 53.5Hz); and a doublet of doublets and a doublet for the bridging-dppm ligand (δP_M 22.0, δP_X 25.2 p.p.m., $^{2}J_{P_MP_X}$ 52.0Hz). The ^{1}H n.m.r. spectrum of (150) shows for the p-cymene ring a complex multiplet between 4.5 and 5.8 p.p.m. and doublet resonances for each methyl group of the isopropyl ring substituent. As with the complexes [(p-cym)RuCl(μ-$SePPh_2$)-(μ-PPh_2)Pt(S_2CNEt_2)] (104) and (166) (see later), the unusually complex resonances are thought to arise from the p-cymene ring(s) adopting a preferred conformation; as a result of steric crowding restricting free rotation of the ring(s).

Similarly, treating [(p-cym)$OsCl_2$]$_2$ with [p-cym)Ru-($PPhEt_2$)(dppe-P)Cl]BPh_4 (137) and [(C_5Me_5)$RhCl_2$]$_2$ with [(C_6H_6)Ru($PPhEt_2$)(dppe-P)Cl]PF_6 (134) in 1:2 molar ratios in $CDCl_3$ provide a route to the heterobimetallics [(p-cym)Ru($PPhEt_2$)Cl(μ-dppe)$OsCl_2$(p-cym)]BPh_4 (151) and [(C_6H_6)Ru($PPhEt_2$)Cl(μ-dppe)$RhCl_2$(C_5Me_5)]PF_6 (154) respectively. These were characterised <u>in situ</u> by $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy.

An alternative type of potentially useful heterobimetallic complex can be prepared by treating [CODIrCl]$_2$ with two equivalents of [(C_6H_6)Ru($PPhMe_2$)(dppm-P)Cl]PF_6 (142) in $CDCl_3$. A rapid reaction occurs to produce the complex [(C_6H_6)Ru($PPhMe_2$)Cl(μ-dppm)IrCl(COD)]PF_6 (152). The complex

$[(p\text{-cym})Ru(PPhEt_2)Cl(\mu\text{-dppe})IrCl(COD)]BPh_4$ (153) was similarly prepared by treating $[CODIrCl]_2$ with $[(p\text{-cym})Ru(PPhEt_2)(dppe\text{-}P)Cl]BPh_4$ (137). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the reaction solutions reveal characteristic first order AMX patterns for (152) and (153). Recovery of complex (152) was achieved with minimal product decomposition by addition of methanol to the reaction solution.

5.5 REACTION OF DIPHOSPHINES WITH $[(arene)MCl_2]_2$ (M=Ru,Os)

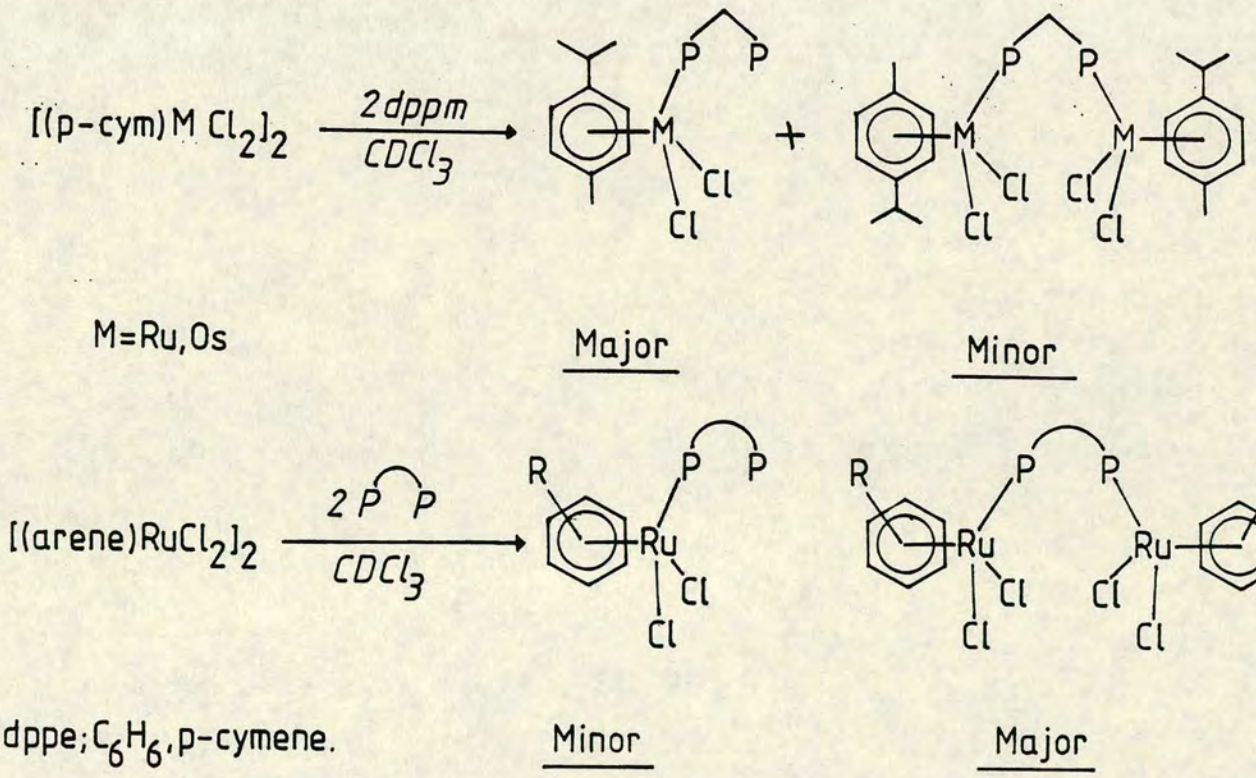
Zelonka and Baird[139] reported that stirring an equimolar ratio of dppm and $[(C_6H_6)RuCl_2]_2$ in acetonitrile for one hour at 45°C produced the complex $[(C_6H_6)RuCl_2(dppm\text{-}P)]$ containing a dangling dppm ligand. Under analogous conditions the diphosphine bridged complex $\{[(C_6H_6)RuCl_2]_2(\mu\text{-dppb})\}$ was prepared from $[(C_6H_6)RuCl_2]_2$ and dppb. Faranone, Loprete and Tresoldi[160] later described the dppe, dppp and diarsine bridged analogues, preferring to prepare these by refluxing an equimolar ratio of $[(C_6H_6)RuCl_2]_2$ and bidentate ligand ($\overset{\frown}{L\ L}$) in benzene for two hours. Refluxing $[(C_6H_6)RuCl_2]_2$ with 2 equivalents of $\overset{\frown}{L\ L}$ in ethanol for 50 mins produced the monocationic complexes $[(C_6H_6)RuCl(\overset{\frown}{L\ L})]Cl$ containing the bidentate chelate. The chelate complexes were also prepared by refluxing $\{[(C_6H_6)RuCl_2]_2(\mu\text{-}\overset{\frown}{L\ L})\}$ with a further equivalent of $\overset{\frown}{L\ L}$ in ethanol for 1 hour.

It was felt a reinvestigation of the reactions of $[(arene)RuCl_2]_2$ with diphosphines was justified to gain further information on these systems and hopefully to detect

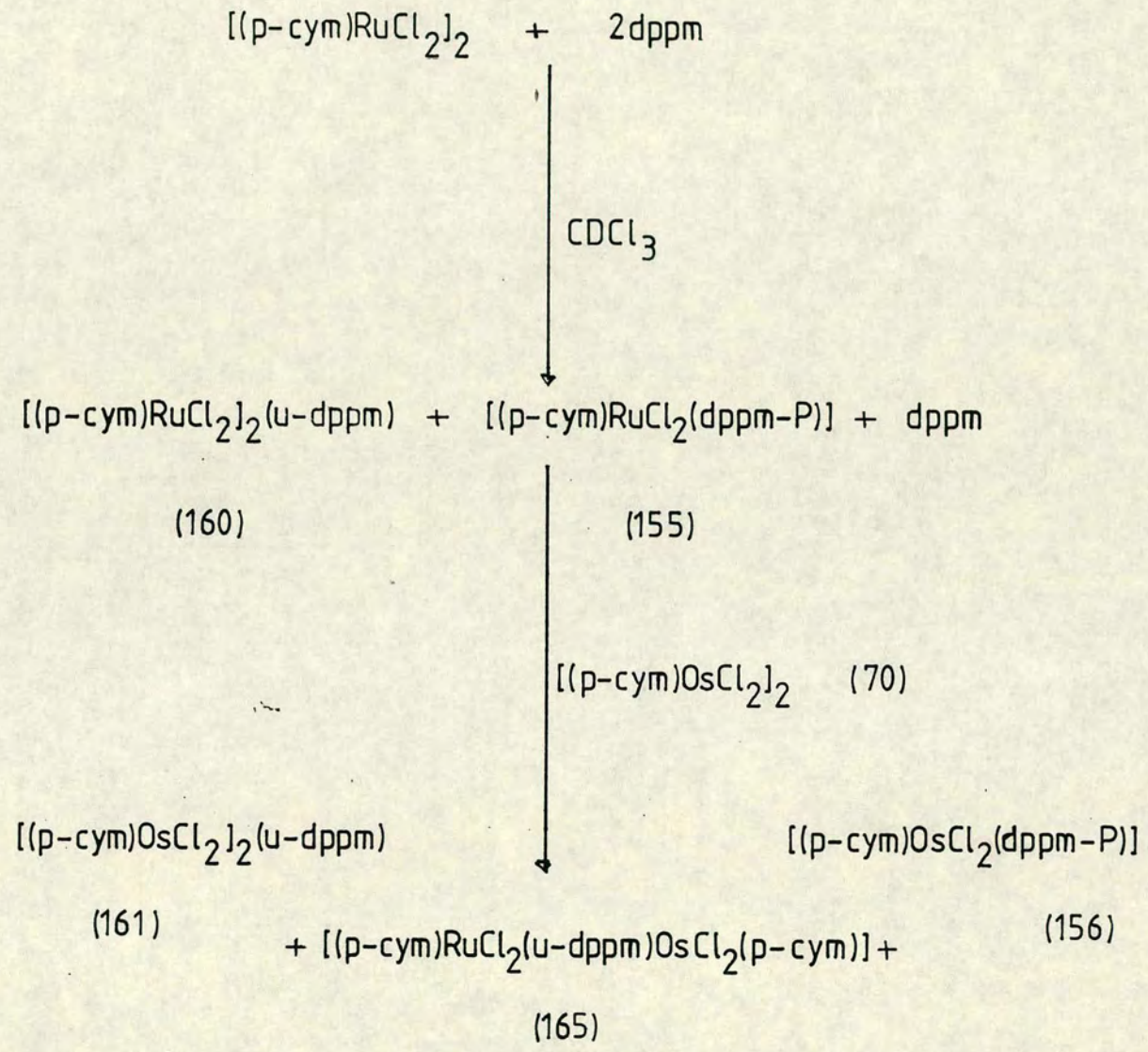
additional examples of mononuclear complexes containing dangling diphosphine ligands. The work took advantage of readily accessible $^{31}P-\{^{1}H\}$ n.m.r. facilities with reactions examined on a n.m.r. tube scale. With the exception of $[(C_6H_6)RuCl_2(dppm-P)]$[140] the $^{31}P-\{^{1}H\}$ n.m.r. parameters for the complexes described in this section are reported for the first time.

Both the 1:1 and 1:2 molar reactions of $[(arene)RuCl_2]_2$ (arene = C_6H_6,p-cymene) and diphosphine (dppm,dppe,dppp) proceed rapidly at room temperature to give monometallic dangling and/or bimetallic bridged diphosphine complexes without having to use either refluxing conditions or ionising solvents. If $[(p\text{-}cym)RuCl_2]_2$ is mixed with two equivalents of dppm in $CDCl_3$ the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the reaction solution shows that two metal diphosphine species are produced. The major product, showing two doublet resonances (δP 25.7, -27.7 p.p.m., $^{2}J_{PP}$ 33.0Hz), is identified as the dangling dppm complex $[(p\text{-}cym)RuCl_2(dppm-P)]$ (155). The minor product, which gives a singlet resonance in the region typical of P bound to Ru (δP 20.8 p.p.m.), is assigned as the dppm bridged complex $\{[(p\text{-}cym)RuCl_2]_2(\mu\text{-}dppm)\}$ (160). A similar result is obtained for the reaction of $[(p\text{-}cym)OsCl_2]_2$ with two equivalents of dppm. An attempt to prepare $[(C_6H_6)RuCl_2(dppm-P)]$ by the method of Zelonka and Baird[139] gave predominantly the bridged complex $\{[(C_6H_6)RuCl_2]_2(\mu\text{-}dppm)\}$. The 1:2 molar reaction of $[(arene)RuCl_2]_2$ and either dppe or dppp in $CDCl_3$ also gives rise to a mixture of dangling and bridging diphosphine complexes with the bridging

complex dominating as the major reaction product [Scheme 16]. The lower solubility of the bimetallic complexes in $CHCl_3$ can be used as a crude means of separating the mixtures. However direct use of the reaction mixture containing the dangling diphosphine complex provided a useful route to a new heterobimetallic complex. $[(p\text{-cym})RuCl_2]_2$ was treated with two equivalents of dppm in $CDCl_3$ to generate a mixture of $[(p\text{-cym})RuCl_2(dppm\text{-}P)]$ (155), $\{[(p\text{-cym})RuCl_2]_2(\mu\text{-dppm})\}$ (160) and unreacted dppm. $[(p\text{-cym})OsCl_2]_2$ was then added to the mixture to give a Ru:Os ratio of 1:1. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed signals for five metal diphosphine complexes, including the heterobimetallic complex $[(p\text{-cym})RuCl_2(\mu\text{-dppm})OsCl_2(p\text{-cym})]$ (165) (δP 19.4, -20.5 p.p.m., $^2J_{PP}$ 48.4Hz) [Scheme 17].



Scheme 16: Reaction of $[(arene)MCl_2]_2$ with diphosphines

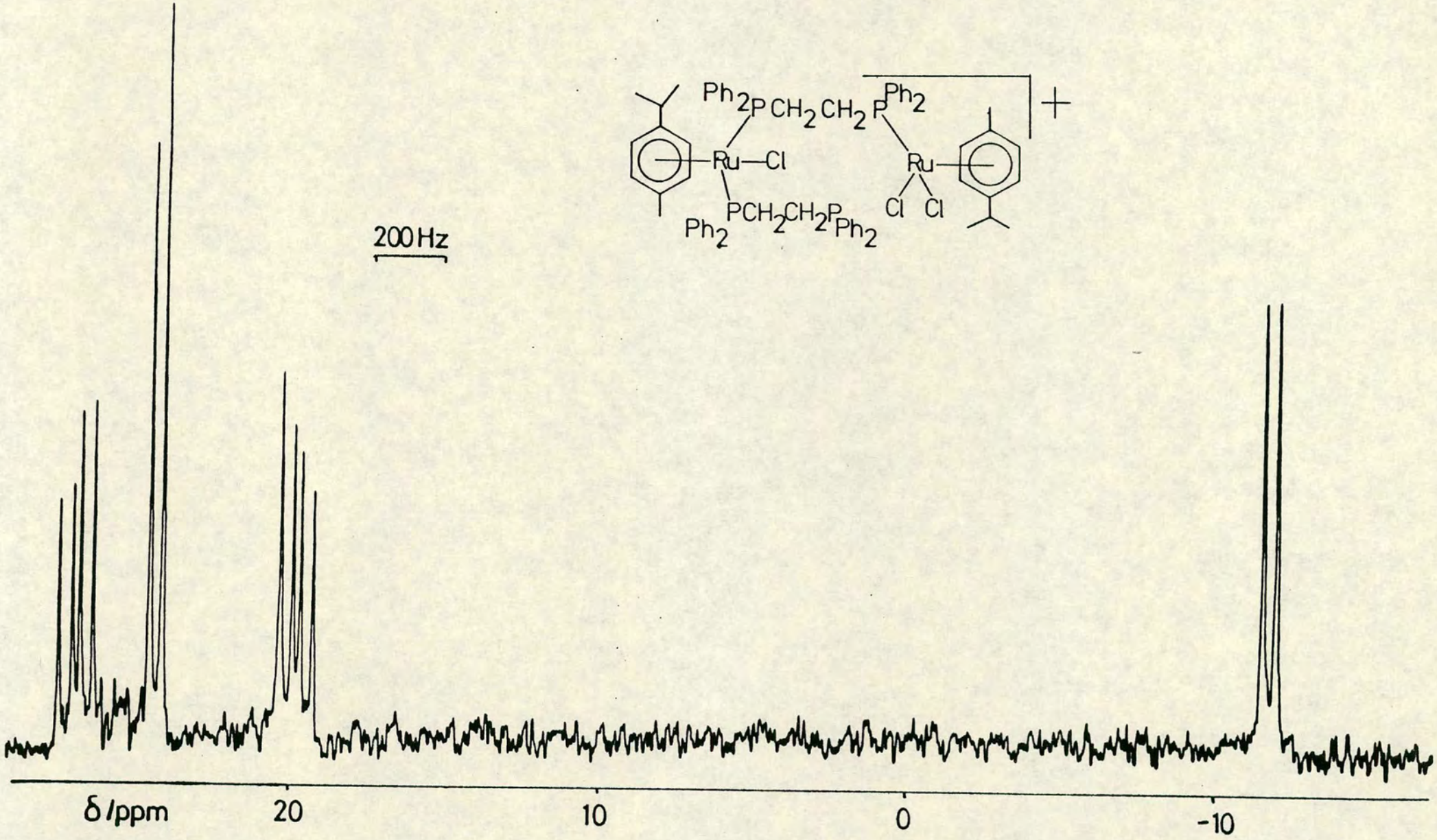


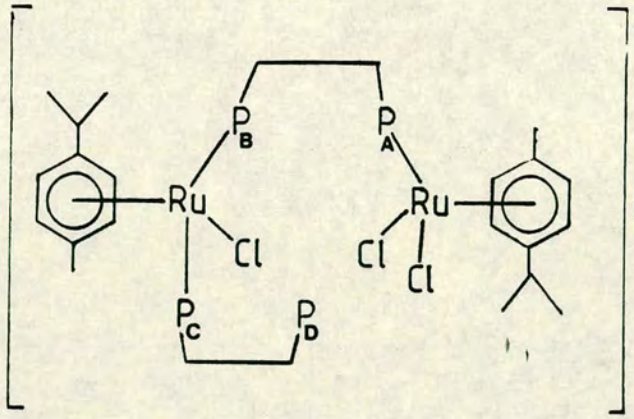
Scheme 17: Formation of the heterobimetallic complex [(p-cym)$RuCl_2$(μ-dppm)$OsCl_2$(p-cym)] (165)

The homobimetallic complexes {[(arene)$RuCl_2$]$_2$(μ-diphosphine)} (160-164) can be prepared in high yield by mixing equimolar quantities of [(arene)$RuCl_2$]$_2$ and diphosphine in CH_2Cl_2 at room temperature.

Previously it was shown that under suitable conditions treatment of monophosphine complexes of the type [(arene)$RuCl_2(PR_3)$] with a range of diphosphines produced the monometallic compounds [(arene)$Ru(PR_3)$-(diphosphine-P)Cl]Y (136-145). Similarly the equimolar reaction of {[(p-cym)$RuCl_2$]$_2$(μ-dppe)} (162) (which can be considered as a more complex member of the [(arene)$RuCl_2$-(PR_3)] genre) and dppe in a mixed $MeOH/CH_2Cl_2$ solvent in the presence of either $NaBPh_4$ or NH_4PF_6 produces the bimetallic complex [(p-cym)$RuCl_2$(μ-dppe)RuCl(p-cym)(dppe-P)]Y (166) containing both bridging and dangling dppe ligands. The high resolution $^{31}P-\{^1H\}$ n.m.r. spectrum of (166, Y = BPh_4) [Figure 31] consists of four separate resonances, three in the region typical of P bound to Ru (P_A,P_B,P_C) and the fourth (P_D) at a position characteristic of an uncoordinated P atom of a dangling dppe ligand. Resonance splittings are derived from $^2J_{PP}$ and/or $^3J_{PP}$ couplings with the P_B and P_C signals appearing as doublets of doublets and the P_A and P_D signals as simple doublets. In the ^1H n.m.r. spectrum of (166) a highly complex pattern results for the arene ring protons and each methyl group of the isopropyl ring substituent appears as a doublet resonance. This suggests that free rotation of the p-cymene ring is restricted (as in (104) and (150)) due to steric crowding at each metal associated with the bulky aryl and alkyl substituents on phosphorus.

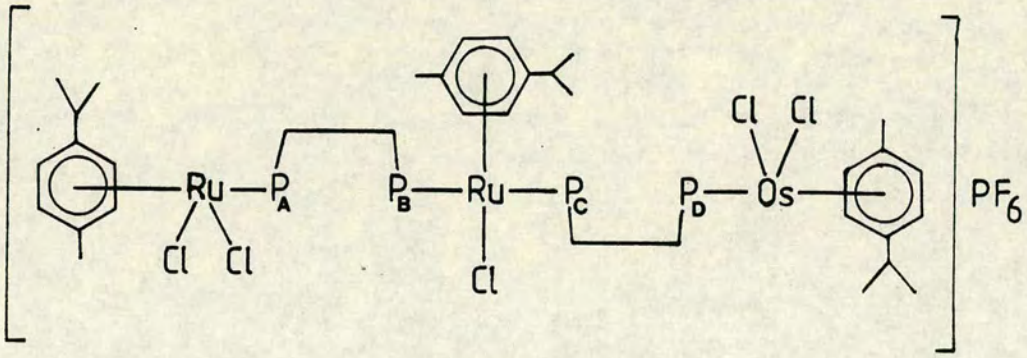
Figure 31 The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of [(p-cymene)$RuCl_2$(μ-dppe)RuCl-(p-cymene)(dppe-P)]BPh_4 (166) in $CDCl_3$ at 298°K





δP_A 24.2ppm $^3J_{P_AP_B}$ 33.0Hz
δP_B 19.3ppm
δP_C 26.9ppm $^2J_{P_BP_C}$ 53.4Hz
δP_D -12.7ppm $^3J_{P_CP_D}$ 34.6Hz

(166)



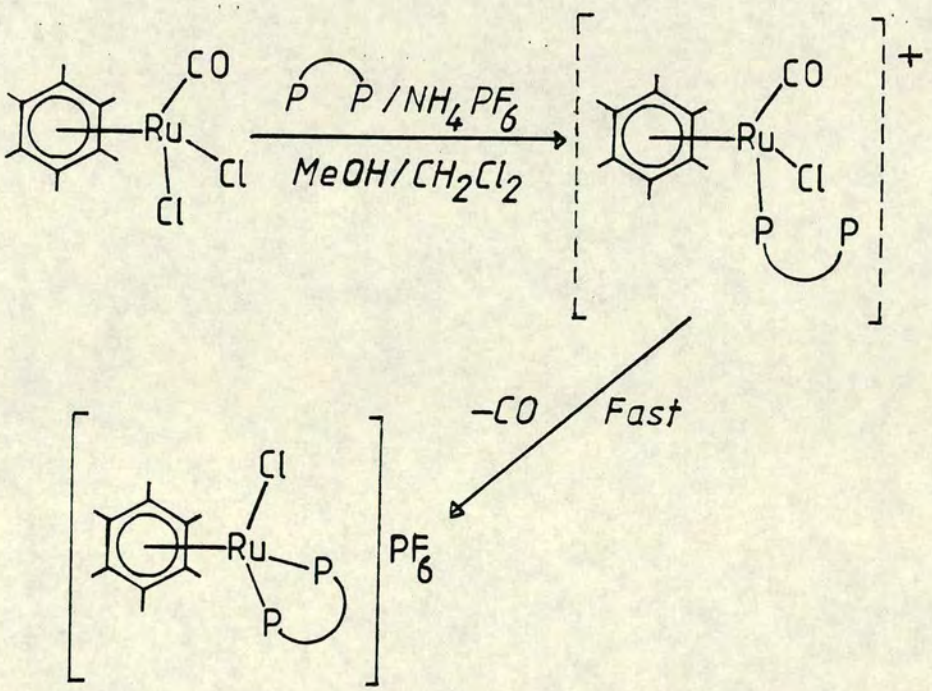
(167)

δP_A 25.3ppm δP_B 22.5ppm δP_C 24.1ppm δP_D -15.6ppm
$^2J_{P_AP_B}$ 27.2Hz $^3J_{P_BP_C}$ 53.4Hz $^2J_{P_CP_D}$ 27.1Hz

The dangling P_D atom in (166) can be used as a site to bind a further metal fragment. Treatment of $[(p\text{-cym})OsCl_2]_2$ with 2 equivalents of (166) in CD_2Cl_2 produces the 'dppe-chain' trimetallic complex $[(p\text{-cym})RuCl_2(\mu\text{-dppe})RuCl(p\text{-cym})(\mu\text{-dppe})OsCl_2(p\text{-cym})]PF_6$ (167), which has been characterised by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy.

The monocationic complex $[(C_6H_6)Ru(dppe\text{-}P,P)Cl$ (168) was prepared by the literature method.[160] Attempts to

produce the complex $[(C_6H_6)Ru(dppe\text{-}P,P)(dppe\text{-}P)]Y_2$ by reacting (168) with dppe in the presence of chloride scavengers, such as NH_4PF_6, $TlBF_4$ or $AgBF_4$, were unsuccessful. This is slightly surprising given the 'routine' preparation or tris(phosphine) complexes such as $[(C_6H_6)Ru(PMe_3)(PMePh_2)(PPh_3)][PF_6]_2$ by Werner,[154] although similar to the result reported by Robertson for the unsuccessful reaction of $[(C_6H_6)Ru(1,10\text{-Phen})Cl]PF_6$ and dppe.[158] A reaction was observed on treating (168) with NaS_2CNEt_2 in CH_3CN although the product was not identified. The diphosphine chelate complexes $[(C_6Me_6)Ru(diphosphine\text{-}P,P)Cl]PF_6$ ((169) dppm, (170) dppe, (171) dppp) were produced by 'default' in the room-temperature reaction of $[(C_6Me_6)RuCl_2CO]$ with diphosphine [Equation 45].



(169-171)

---------[45]

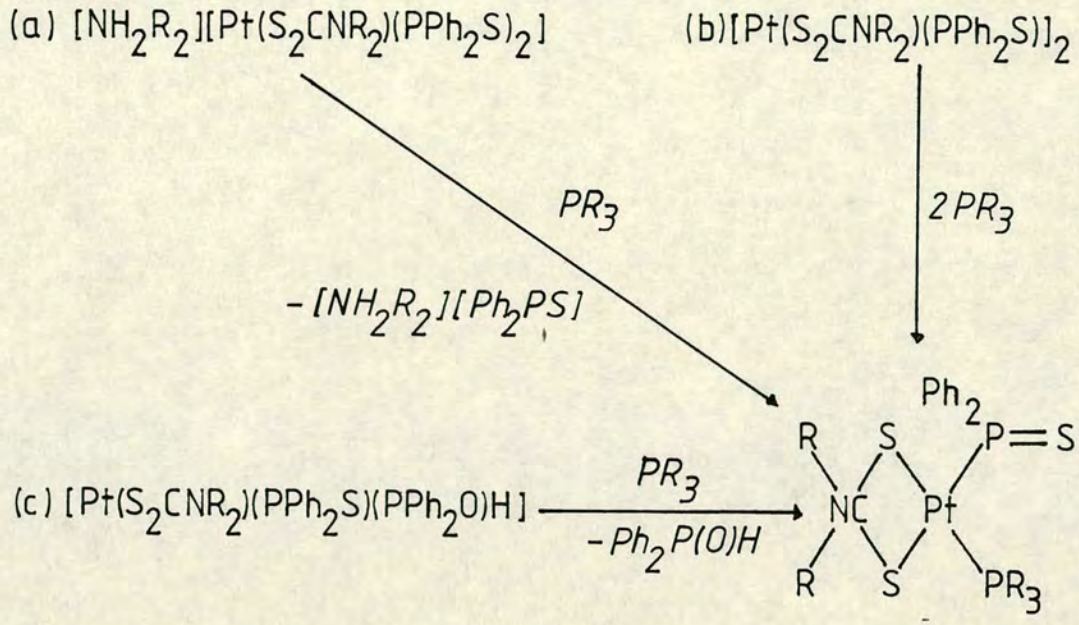
It is likely that formation of the chelate complex (169-171) occurs via the undetected dangling diphosphine intermediate $[(C_6Me_6)Ru(CO)(\text{diphosphine-P})Cl]^+$. This intermediate species might be detectable at lower temperatures since the stable complex $[(C_6Me_6)Ru(CO)(PMe_3)Cl]PF_6$ has been reported.[148]

Kang, Moseley and Maitlis[97] reported that refluxing an equimolar ratio of $[(C_5Me_5)RhCl_2]_2$ and dppe in ethanol for 2 hours produced the bridged bimetallic $\{[(C_5Me_5)RhCl_2]_2(\mu\text{-dppe})\}$. Refluxing for 5 hours with excess dppe produced the chelate complex $[(C_5Me_5)Rh(\text{dppe-P,P})Cl_2]$, which on treatment with aqueous NH_4PF_6 gave the chelate salt $[(C_5Me_5)Rh(\text{dppe-P,P})Cl]PF_6$ (177). Refluxing conditions to promote the reaction of $[(C_5Me_5)RhCl_2]_2$ and diphosphine are in fact unnecessary. The 2:1 molar reaction of dppe and $[(C_5Me_5)RhCl_2]_2$ in CH_2Cl_2 at room temperature proceeds rapidly to give a mixture of the dangling and bridging dppe complexes $[(C_5Me_5)Rh(\text{dppe-P})Cl_2]$ (174) and $\{[(C_5Me_5)RhCl_2]_2(\mu\text{-dppe})\}$. Under analogous conditions reaction of $[(C_5Me_5)RhCl_2]_2$ and dppm gives exclusive formation of the unstable complex $[(C_5Me_5)Rh(\text{dppm-P})Cl_2]$ (175). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the reaction solution reveals that over a 3 hour period the characteristic set of signals for the dangling dppm complex (175) (δP 30.8, $^1J_{RhP}$ 141.0, $^2J_{PP}$ 28.1; δP -25.8 p.p.m., $^3J_{RhP}$ 4.3Hz) is replaced by a doublet resonance (δP -4.8 p.p.m., $^1J_{RhP}$ 114.4Hz) which is assigned to the dppm chelate complex $[(C_5Me_5)Rh(\text{dppm-P,P})Cl]Cl$ (176)

The equimolar reaction of $[(C_5Me_5)RhCl_2(PPh_3)]$ and dppe in a mixed $MeOH/CH_2Cl_2$ solvent in the presence of NH_4PF_6 gives, after stirring the reaction solution for 24 hours, a solid identified as the chelate complex $[(C_5Me_5)Rh(dppe\text{-}P,P)Cl]PF_6$ (177). If the same reaction is performed in the presence of $NaBPh_4$ instead of NH_4PF_6 an orange solid is deposited from the reaction solution after 5 mins. The solid gives a complicated $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum consistent with the formation of the dangling dppe complex $[(C_5Me_5)Rh(PPh_3)(dppe\text{-}P)Cl]BPh_4$. Over a period of several hours the spectrum reveals the concomitant growth of a singlet (δP -4.1 p.p.m.) and doublet (δP 64.7 p.p.m., $^1J_{RhP}$ 131.8Hz) resonance associated with loss of PPh_3 from the dangling dppe complex and formation of the dppe chelate complex $[(C_5Me_5)Rh(dppe\text{-}P,P)Cl]BPh_4$.

5.6 PREPARATION OF COMPLEXES OF THE TYPE $[Pt(S_2CNR_2)(Ph_2PS)(PR_3)]$

Anderson[5] identified the species $[Pt(S_2CNEt_2)(PPhMe_2)]$ as an intermediate in the equimolar reaction of $[NH_2Et_2][Pt(S_2CNEt_2)(Ph_2PS)_2]$ and $[Ru(PPhMe_2)_4(CH_3CO_2)]PF_6$ to produce the complexes $[Ru(\eta^2\text{-}Ph_2PS)_2(PPhMe_2)_2]$ and $[Pt(S_2CNEt_2)(PPhMe_2)_2]^+$. High yield routes to complexes of the type $[Pt(S_2CNR_2)(Ph_2PS)(PR_3)]$ (178-181) have now been developed[183] [Equation 46].



Prep.

(a) $[Pt(S_2CN^iPr_2)(Ph_2PS)(PPhMe_2)]$(178)

(a) $[Pt(S_2CN^iPr_2)(Ph_2PS)(PPhEt_2)]$(179)

Prep.

(b) $[Pt(S_2CNEt_2)(Ph_2PS)(PPhMe_2)]$(180)

(c) $[Pt(S_2CNEt_2)(Ph_2PS)(PPh_3)]$(181)

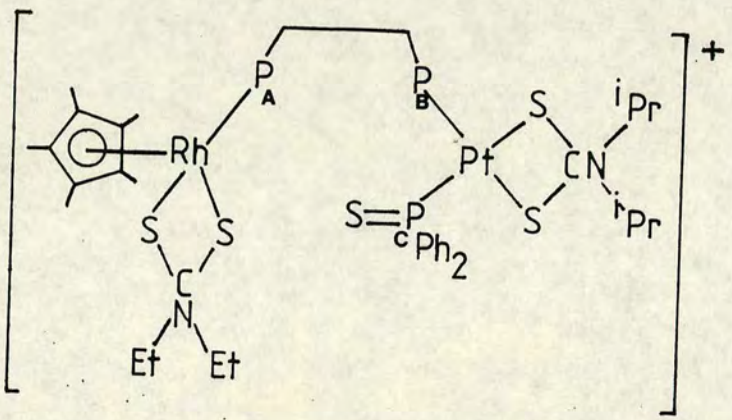
-----[46]

The reactants are stirred in either chloroform or benzene at room temperature for one hour. The product (178-181) can then be recovered as a pale yellow solid on addition of Et_2O to the reaction solution. The $^{31}P-\{^1H\}$ n.m.r. spectra for the complexes (178-181) consist of two sets of 1:4:1 triplet of doublets resonances and are consistent with inequivalent P atoms cis-bound to Pt. The i.r. spectra for the isolated solids show strong bands for ν_{CN} (1490-1510 cm^{-1}) and ν_{PS} (600-610 cm^{-1}).

One facet of the chemistry of the dangling diphosphine complexes prepared in Sections 4.2 and 5.2 is that they function as 'tertiary phosphine' ligands.

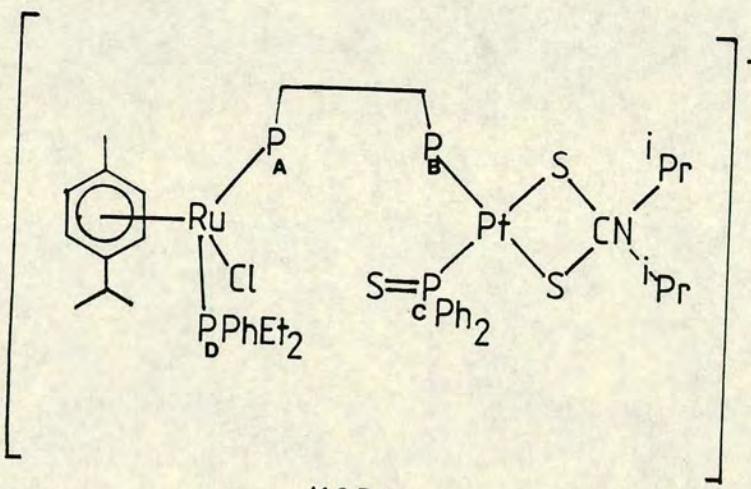
The equimolar reaction of either $[(C_5Me_5)Rh(S_2CNEt_2)$-

(dppe-P)]BPh_4 (109) or [(p-cym)Ru($PPhEt_2$)(dppe-P)Cl]BPh_4 (137) with [$NH_2{}^iPr_2$][Pt($S_2CN^iPr_2$)(Ph_2PS)$_2$] (6) in $CDCl_3$ at room temperature gives immediate formation of the singly bridged dppe heterobimetallics [(C_5Me_5)Rh(S_2CNEt_2)(μ-dppe)-Pt(Ph_2PS)($S_2CN^iPr_2$)]BPh_4 (182) and [(p-cym)Ru($PPhEt_2$)-Cl(μ-dppe)Pt(Ph_2PS)($S_2CN^iPr_2$)]BPh_4 (183), which have been characterised by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. The KBr disc i.r. spectrum of (182), recovered as an orange solid on addition of methanol to the reaction solution, shows bands for ν_{CN} (1503 and 1512 cm^{-1}) and ν_{PS} (610 cm^{-1}).



(182)

δP_A	34.0ppm
δP_B	10.6ppm
δP_C	26.4ppm
$^1J_{PtP_B}$	3503.4Hz
$^1J_{PtP_C}$	3085.5Hz
$^4J_{PtP_A}$	13.2Hz
$^1J_{RhP_A}$	145.2Hz
$^2J_{P_BP_C}$	25.3Hz
$^3J_{P_AP_B}$	25.3Hz



(183)

δP_A	26.8ppm
δP_B	10.3ppm
δP_C	26.6ppm
δP_D	18.9ppm
$^1J_{PtP_B}$	3511.9Hz
$^1J_{PtP_C}$	3087.6Hz
$^2J_{P_BP_C}$	25.5Hz
$^2J_{P_AP_D}$	51.0Hz
$^3J_{P_AP_B}$	29.8Hz

5.7 CONCLUSIONS

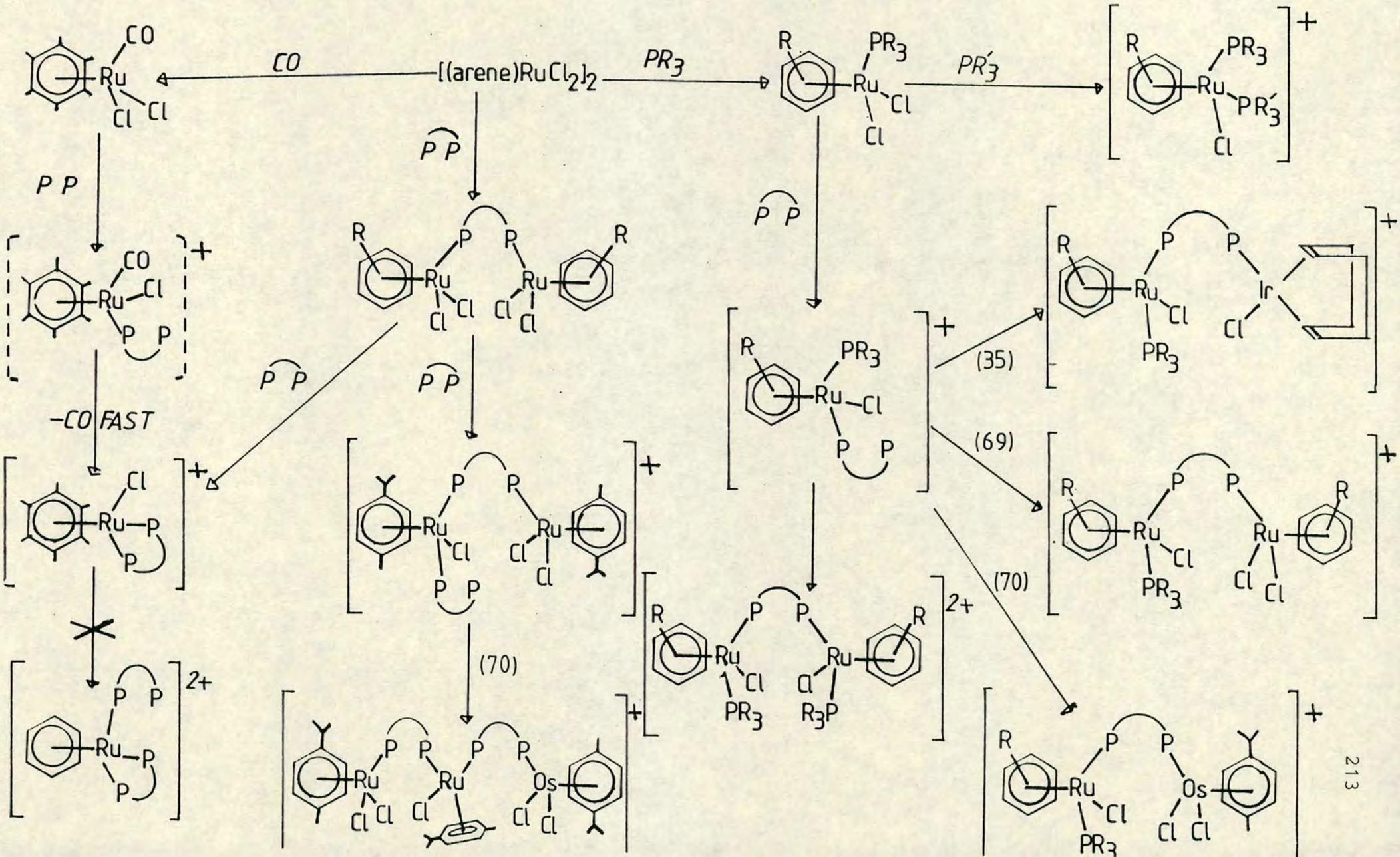
A rational and relatively straightforward method for the preparation of homo- and hetero-bimetallics has been devised. The method involves the use of mononuclear complexes containing a single dangling-diphosphine ligand. These act essentially as exotic tertiary phosphine ligands during reaction. It is anticipated that the 'phosphine-metal' ligands could be used successfully for reactions in coordination chemistry already developed for conventional tertiary phosphine ligands to provide a large number of new types of multimetallic systems. In contrast to the hetero-bimetallics produced in Chapter 4, the bimetallics produced in this chapter retain potentially reactive sites on both metals. Unfortunately time was not available to investigate their chemistry further.

Complexes of the type $[(arene)RuCl(PR_3)(PR_3')]PF_6$ (135) have been shown to undergo a two electron reduction with $NaC_{10}H_8$ to give the highly reactive, electron rich species $[(arene)Ru(PR_3)(PR_3')$ [150] (Scheme 9). An investigation of the nature and reactivity of the products obtained on reduction of the compounds $[(arene)Ru(PR_3)(diphosphine\text{-}P)Cl]Y$ (136-145), $\{[(arene)MCl(PPhMe_2)]_2(\mu\text{-diphosphine})\}[PF_6]_2$ (146-149) and (150-155) should be considered. In addition an investigation of the substitution reactions involving the terminal chloride and 1,5-COD ligands in the complexes (150-154) and the possibility of introducing a second bridging ligand to hold the metal centres in close proximity would be of interest.

Complexes of the type $[(OC)_4M(\mu\text{-diphosphine})_2M'(CO)_4]$ have been prepared for the metals Cr, Mo and W.[217,218] An attempt could be made to coordinate the dangling P atom in the complex $[(p\text{-cym})RuCl_2(\mu\text{-dppe})RuCl(p\text{-cym})(dppe\text{-}P)]Y$ (166) to form the bimetallic $[(p\text{-cym})RuCl(\mu\text{-dppe})_2RuCl(p\text{-cym})]Y_2$ and its chemistry, including reduction with $NaC_{10}H_8$, investigated.

A schematic summary of some of the work carried out in Chapter 5 is given in Scheme 18.

Scheme 18 A Schematic Summary of Chapter 5



5.8 EXPERIMENTAL

5.8.1 MATERIALS

The complexes $[(arene)MCl_2]_2$ (M = Ru, arene = C_6H_6, p-cymene, C_6Me_6; M = Os, arene = p-cymene) and $[(C_5Me_5)RhCl_2]_2$ were prepared by standard literature methods.[97,141] The monophosphine derivatives $[(arene)RuCl_2(PR_3)]$ (arene = C_6H_6, PR_3 = $PPhMe_2$, $PPhEt_2$, PPh_3; arene = p-cymene, PR_3 = $PPhMe_2$, $PPhEt_2$, $P(OMe)_3$) and $[(p\text{-}cym)OsCl_2(PPhMe_2)]$ ($^{31}P\text{-}\{^1H\}$ n.m.r. data $CDCl_3$/R.T. δP -33.3 p.p.m.) were prepared by stirring $[(arene)MCl_2]_2$ with a slight excess of the phosphine in CH_3CN at room temperature for 1.5 hours. A reduction in the volume of the reaction solution produced the monophosphine complex as either a red (M = Ru) or yellow (M = Os) microcrystalline solid, which was filtered off, washed with copious amounts of Et_2O and pet ether 40-60° b.p. and dried *in vacuo*. Yield normally in excess of 80%. The diphosphine ligands were obtained from commercial sources.

5.8.2 CRYSTAL DATA FOR $\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppe})\}[PF_6]_2\cdot CH_3NO_2$ (146)

$C_{54}H_{58}Cl_2P_4Ru_2.2PF_6.CH_3NO_2$, M = 1454.92, Monoclinic. a = 28.325(6), b = 9.790(5), c = 23.042(6)Å, β = 105.999(6)°, U = 6142Å^3, Z = 4, D_C 1.573 g cm^{-3}. Space group $I_{2/c}$ (No. 15), Mo-K_α radiation, λ = 0.71069Å, Mu 7.37 cm^{-1}, F(000) = 2720, T = 293°K. The structure solution and refinement were based on 3495 observed ($I > 6\sigma(I)$) reflections (5811 measured) from a Stoe-Stadi 2 diffractometer to give final

R and R_w values of 0.0489 and 0.0688 respectively.

5.8.3 METAL COMPLEXES PREPARED IN CHAPTER 5

[$(C_6H_6)Ru(PPhEt_2)(dppe\text{-}P)Cl]PF_6$ (136). NH_4PF_6 (114 mg, 0.7 mmol) dissolved in methanol (25 ml) was added to a CH_2Cl_2 (5 ml) solution containing [$(C_6H_6)RuCl_2(PPhEt_2)$] (115 mg, 0.28 mmol) and dppe (110 mg, 0.28 mmol). After stirring for several hours at room temperature, the reaction solution became turbid and a yellow solid was gradually deposited. Stirring was continued for 16 hours when the yellow solid was filtered off, washed with ethanol and Et_2O and dried *in vacuo*. On reducing the volume of the pale green filtrate a second batch of yellow product could be recovered. Total yield 197 mg, 76%. Prepared using the same method were [$(C_6H_6)Ru(PPhMe_2)(dppe\text{-}P)Cl]PF_6$ (138). Using [$(C_6H_6)RuCl_2(PPhMe_2)$], dppe and NH_4PF_6. Yield 71%. [$(p\text{-cym})Ru(PPhMe_2)(dppe\text{-}P)Cl]PF_6$ (139). Using [$(p\text{-cym})RuCl_2$-$(PPhMe_2)$], dppe and NH_4PF_6. Yield 75%. [$(C_6H_6)Ru(PPhMe_2)$-$(dppm\text{-}P)Cl]PF_6$ (142). Using [$(C_6H_6)RuCl_2(PPhMe_2)$], dppm and NH_4PF_6. Yield 73%. Found C, 48.4; H, 4.5; N, 1.1; Calc. for $C_{39}H_{39}P_4ClF_6Ru.\frac{1}{2}NH_4PF_6$ C, 48.6; H, 4.5; N, 0.7. ^1H n.m.r. data $CDCl_3$/303°K. $\delta_{C_6H_6}$ 5.86s(6); δ_{Me} 1.94d(3), 1.56d(3), $^2J_{PH}$ 10.4Hz; δ_{CH_2} 3.98 ddd $\delta_{C_6H_5}$ 6.96-7.64 p.p.m. After one day in $CDCl_3$ solution or in an air atmosphere over several weeks, decomposition of the orange product occurs (orange → green colour change) to give an unidentified mixture of species. [$(C_6H_6)Ru(PPhMe_2)(dppp\text{-}P)Cl]PF_6$ (145). Using

$[(C_6H_6)RuCl_2(PPhMe_2)]$, dppp and NH_4PF_6. Yield 61%.
In these reactions the two batches of product were normally treated separately as the first batch of product, obtained directly from the reaction, sometimes contained amounts of the diphosphine-bridged (dppe and dppp only) complexes (146,147,149).

[(p-cym)Ru(PPhEt$_2$)(dppe-P)Cl]BPh$_4$ (137). $NaBPh_4$ (250 mg, 0.73 mmol) dissolved in methanol (25 ml) was added to a CH_2Cl_2 (5 ml) solution containing $[(p\text{-cym})RuCl_2(PPhEt_2)]$ (183 mg, 0.39 mmol) and dppe (154 mg, 0.39 mmol). The reaction solution was stirred at room temperature for 3 hours during which time a large quantity of yellow product precipitated. The yellow product was filtered off, washed with MeOH and Et_2O and dried in vacuo. Yield 0.37 g, 82%. Found: C, 73.7; H, 6.5; Calc. for $C_{70}H_{73}P_3BClRu$, C, 74.8; H, 6.4; ^1H n.m.r. spectrum run in CD_2Cl_2 at 303°K. p-cymene ring $\delta_{C\underline{H}_3}$ 1.04s; $\delta_{CH(C\underline{H}_3)_2}$ 1.15d, 1.07d; $\delta_{C_6\underline{H}_4}$ complex signals 4.74-5.33; $\delta_{CH_2C\underline{H}_3}$ 0.82t, 0.91t; broad complex signals 1.5-3.2 for $\delta_{C\underline{H}_2CH_3}$, $\delta_{C\underline{H}Me_2}$, $\delta_{C\underline{H}_2}$ (dppe); $\delta_{C_6\underline{H}_5}$ 6.85-7.69 p.p.m. broad multiplets. $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum run in CD_2Cl_2 at 303°K; p-cymene ring δ_C 99.4 (3.8)(A), 95.1(2.1)(B), 89.4(9.4)(C), 85.3(9.8)(D), 31.4(E), 22.2 and 20.5(F), 16.3(G). NOTE: Doublet couplings observed on (A-D) carbon resonances (refer to key in Table 11). Single peak 96.2 not assigned. $\delta_{CH_2C\underline{H}_3}$ 9.5(6.5), 8.5(7.3) $\delta_{C\underline{H}_2CH_3}$ and δ_{CH_2} (dppe) assigned to various peaks 18.7-23.0; $\delta_{C_6\underline{H}_5}$ 121.9-137.8 p.p.m. KBr disc i.r. spectrum ν_{RuCl} 310

cm^{-1}. Prepared by the same method were [$(C_6H_6)Ru(PPh_3)$-(dppe-P)Cl]BPh_4 (140). Using [$(C_6H_6)RuCl_2(PPh_3)$], dppe and $NaBPh_4$. Yield 69%. ^1H n.m.r. spectrum run in $CDCl_3$ at 303°K. $\delta_{C_6H_6}$ 5.48; δ_{CH_2} (dppe) 2.45, 1.30; $\delta_{C_6H_5}$ 7.23-7.86 p.p.m. [(p-cym)$Ru(P(OMe)_3)$(dppe-P)Cl]BPh_4 (141). Using [(p-cym)$RuCl_2(P(OMe)_3)$], dppe and $NaBPh_4$. Yield 78%. [(p-cym)$Ru(P(OMe)_3)$(dppm-P)Cl]BPh_4 (144). Using [(p-cym)-$RuCl_2(P(OMe)_3)$], dppm and $NaBPh_4$, Yield 71%.

{[$(C_6H_6)RuCl(PPhMe_2)$]$_2$(μ-dppe)}$[PF_6]_2$ (146). NH_4PF_6 (180 mg, 1.1 mmol) dissolved in methanol (25 ml) was added to a CH_2Cl_2 (5 ml) solution containing [$(C_6H_6)RuCl_2(PPhMe_2)$] (210 mg, 0.54 mmol) and dppe (108 mg, 0.27 mmol). The reaction solution was stirred at room temperature for 20 hours during which time the yellow product was deposited. The yellow product was filtered off, washed with methanol and Et_2O and dried *in vacuo*. A second batch of product could be recovered on reducing the volume of the light-red filtrate. Total yield 83%. M.p. 195°C (decomposition). Found (crystals) C, 44.7; H, 4.2; N, 1.3; Calc. for $C_{54}H_{58}P_6Cl_2F_{12}Ru_2.CH_3NO_2$; C, 45.0; H, 4.2; N, 1.0. ^1H n.m.r. spectrum run in CD_3NO_2 at 303°K. $\delta_{C_6H_6}$ 5.67, δ_{CH_3} 1.22d, 1.50d, $^2J_{PH}$ 10.7Hz, $\delta_{C_6H_5}$ 7.24-7.72 p.p.m. δ_{CH_2} (dppe) not assigned. Prepared by the same method were {[(p-cym)$RuCl(PPhMe_2)$]$_2$-(μ-dppe)}$[PF_6]_2$ (147). Using [(p-cym)$RuCl_2(PPhMe_2)$], ½ dppe and NH_4PF_6. Yield 80%. Found: C, 49.2; H, 4.94; Calc. for $C_{62}H_{74}P_6Cl_2F_{12}Ru_2$ C, 49.4; H, 4.95. Conductance study in CH_3NO_2, Slope $\Lambda_\infty - \Lambda_e$ against $C_c^{\frac{1}{2}}$ 610, 2:1 electrolyte. {[(p-cym)$OsCl(PPhMe_2)$]$_2$(μ-dppe)}$[PF_6]_2$ (148). Using

$[(p\text{-cym})OsCl_2(PPhMe_2)]$, ½ dppe and NH_4PF_6. The reaction solution was refluxed for 6 hours to produce the pale yellow product. Yield 43%. {[$(C_6H_6)RuCl(PPhMe_2)]_2$-(μ-dppp)}$[PF_6]_2$ (149). Using $[(C_6H_6)RuCl_2(PPhMe_2)]$, ½ dppp and NH_4PF_6. Yield 58%.

[(p-cym)Ru($PPhMe_2$)Cl(μ-dppm)$RuCl_2$(p-cym)] (150). $[(p\text{-cym})RuCl_2]_2$ (20 mg, 0.033 mol) and [(p-cym)Ru($PPhMe_2$)-(dppm-P)Cl]BPh_4 (143) (73 mg, 0.0165 mmol) were mixed in $CDCl_3$ (2 ml) at room temperature. Addition of methanol (10 ml) to the reaction solution precipitated the product as a red solid. Yield 67 mg, 72%. ^1H n.m.r. spectrum run in CD_2Cl_2 at 298°K. p-cymene rings: δ_{CH_3} 0.67s(3), 1.73s(3), $\delta_{CH(Me)_2}$ 2.31sep(1), 2.63sep(1), $\delta_{CH(CH_3)_2}$ 0.92d(3), 1.00d(3), 1.11d(3), 1.22d(3), $^3J_{HH}$ 6.9Hz, $\delta_{C_6H_4}$ complicated 4.65-5.82; δ_{CH_3} ($PPhMe_2$) 1.25d(3), $^2J_{PH}$ 10.5Hz, 1.41d(3), $^2J_{PH}$ 10.1Hz; δ_{CH_2} (dppm) 4.57 p.p.m. (2)d, $\delta_{C_6H_5}$ 6.82-7.91 p.p.m. (45) broad multiplets.

[(p-cym)Ru($PPhEt_2$)Cl(μ-dppe)$OsCl_2$(p-cym)]BPh_4 (151). Generated in situ by mixing $[(p\text{-cym})OsCl_2]_2$ (10 mg) with two equivalents of [(p-cym)Ru($PPhEt_2$)(dppe-P)Cl]BPh_4 (137) (29 mg) in $CDCl_3$ at room temperature. [(C_6H_6)Ru($PPhMe_2$)-Cl(μ-dppm)IrCl(COD)]PF_6 (152). Generated in situ by mixing $[CODIrCl]_2$ (12 mg) with two equivalents of [(C_6H_6)Ru-($PPhMe_2$)(dppm-P)Cl]PF_6 (142) (31 mg) in $CDCl_3$ at room temperature. [(p-cym)Ru($PPhEt_2$)Cl(μ-dppe)IrCl(COD)]BPh_4 (152). Generated in situ by mixing $[CODIrCl]_2$ (11 mg) with two equivalents of [(p-cym)Ru($PPhEt_2$)(dppe-P)Cl]BPh_4 (137) (39 mg) in $CDCl_3$ at room temperature. [(C_6H_6)Ru($PPhEt_2$)-Cl(μ-dppe)$RhCl_2(C_5Me_5)$]PF_6 (154). Generated in situ by

mixing $[(C_5Me_5)RhCl_2]_2$ (12 mg) with two equivalents of $[(C_6H_6)Ru(PPhEt_2)(dppe\text{-}P)Cl]PF_6$ (136) (34 mg) in $CDCl_3$ at room temperature. $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum δP_M 24.6, δP_X 30.1, δP_A 22.8 p.p.m., $^3J_{P_MP_X}$ 31.9, $^2J_{P_AP_M}$ 54.8, $^1J_{RhP_X}$ 145.8Hz.

The dangling diphosphine complexes (155-159, 174-175) were generated, usually along with the corresponding bridging diphosphine complex, by mixing the complex of type $[(ring)MCl_2]_2$ with two equivalents of the diphosphine in $CDCl_3$ at room temperature.

{[(p-cym)RuCl$_2$]$_2$(μ-dppm)} (160). $[(p\text{-cym})RuCl_2]_2$ (199 mg, 0.32 mmol) and dppm (125 mg, 0.32 mmol) were stirred in CH_2Cl_2 (15 ml) at room temperature for 15 minutes. The red reaction solution was reduced in volume and Et_2O added to precipitate the red solid, which was filtered off, washed with Et_2O and pet ether 40-60° b.p. and dried *in vacuo*. Yield 310 mg, 96%. Found C, 53.1; H, 5.10; Calc. for $C_{45}H_{50}P_2Cl_4Ru_2$ C, 54.2; H, 5.1, ^1H n.m.r. spectrum run in $CDCl_3$ at 303°K: p-cymene ring δ_{CH_3} 1.88s(6), δ_{CHMe_2} 2.45sep(2), $\delta_{CH(CH_3)_2}$ 0.92d(12), $^3J_{HH}$ 6.9Hz, $\delta_{C_6H_4}$ 5.00 centre AB(8), J_{HH} 6.2Hz, $\Delta\delta$46.8Hz, δ_{CH_2}(dppm) 4.7t(2), $\delta_{C_6H_5}$ 7.0-7.6 p.p.m. (20) broad multiplets. Prepared by the same methods were {[(p-cym)RuCl$_2$]$_2$(μ-dppe)} (162). Using equimolar quantities of $[(p\text{-cym})RuCl_2]_2$ and dppe. Yield 96%. {[(p-cym)OsCl$_2$]$_2$(μ-dppe)} (161). Using equimolar quantities of $[(p\text{-cym})OsCl_2]_2$ and dppe. Yield 91%. {$[(C_6H_6)RuCl_2]_2$-(μ-dppe)} (163). Using equimolar quantities of $[(C_6H_6)RuCl_2]_2$ and dppe. Yield 95%. {[(p-cym)RuCl$_2$]$_2$-

(μ-dppp)} (164). Using equimolar quantities of $[(p\text{-cym})RuCl_2]_2$ and dppp. Yield 90%.

{[(p-cym)$RuCl_2$(μ-dppe)RuCl(p-cym)(dppe-P)]}Y (166) (Y = BPh_4^-, PF_6^-). $NaBPh_4$ (56 mg, 0.16 mmol) dissolved in methanol (25 ml) was added to a CH_2Cl_2 (5 ml) solution containing {$[(p\text{-cym})RuCl_2]_2$(μ-dppe)} (162) (64 mg, 0.063 mmol) and dppe (28 mg, 0.07 mmol). The reaction solution was stirred at room temperature for 2 hours during which time the product was deposited as a pale red solid. The solid was filtered off, washed with MeOH and Et_2O and dried *in vacuo*. Yield 82 mg, 77%. The PF_6^- salt of (166) was prepared following the above preparative route using NH_4PF_6 and stirring for 18 hours to produce the light-red product. Yield 60%. M.p. 188°C. ^1H n.m.r. spectrum run in $CDCl_3$ at 303°K. p-cymene rings, δ_{CH_3} 0.43s, 1.93s, δ_{CHMe_2} 2.52dsept., $\delta_{CH(CH_3)_2}$ 0.83d, 1.07d, 1.13d, 1.22d, $^3J_{HH}$ 0.9Hz, $\delta_{C_6H_4}$ 4.52-6.07 complex set of signals (distinctive resonances 4.55t, 6.06d); δ_{CH_2} (dppe) 2.44, 3.03, 3.49 broad humps; $\delta_{C_6H_5}$ 6.75-7.85 p.p.m. broad multiplets. $^{31}P\text{-}\{^1H\}$ n.m.r. data refer to text. [(p-cym)$RuCl_2$(μ-dppe)RuCl(p-cym)(μ-dppe)-$OsCl_2$(p-cym)]PF_6 (167). Generated *in situ* by mixing [(p-cym)$RuCl_2$(μ-dppe)RuCl(p-cym)(dppe-P)]PF_6 (166) (40 mg, 0.024 mmol) and $[(p\text{-cym})OsCl_2]_2$ (10 mg, 0.013 mmol) in $CDCl_3$ at room temperature. $^{31}P\text{-}\{^1H\}$ n.m.r. data: refer to text.

The chelating diphosphine complexes [(C_6Me_6)Ru(diphosphine-P,P)Cl]PF_6 (169) dppm, (170) dppe, (180) dppp were prepared by mixing equimolar quantities of [$(C_6Me_6)RuCl_2CO$] and diphosphine in a CH_2Cl_2/MeOH mixed solvent at room

temperature in the presence of NH_4PF_6. An immediate evolution of gas was observed with the product recovered as a red solid on reducing the volume of the reaction solution. Yield 86%. KBr disc i.r. spectra show ν_{RuCl} 300 cm^{-1}.

[$(C_5Me_5)Rh(dppe\text{-}P,P)Cl]PF_6$ (177). Prepared by stirring [$(C_5Me_5)RhCl_2(PPh_3)$] (134 mg, 0.23 mmol) and dppe (94 mg, 0.23 mmol) in CH_2Cl_2/MeOH (5:30 ml) for 14 hours at room temperature in the presence of NH_4PF_6 (50 mg, 0.31 mmol). On reducing the volume of the reaction solution the product was recovered as a bright orange solid. Yield 150 mg, 82%. Found C, 53.1; H, 4.9; Calc. for $C_{36}H_{39}P_3F_6ClRh$ C, 52.9; H, 4.8. ^1H n.m.r. spectrum run in $CDCl_3$ at 303°K. $\delta_{C_5Me_5}$ 1.47td, $^4J_{PH}$ 3.4, $^3J_{RhP}$ 0.36Hz; δ_{CH_2}(dppe) 2.49, 3.06 multiplets, $\delta_{C_6H_5}$ 7.01-7.63 p.p.m. broad multiplets. Use of $NaBPh_4$ instead of NH_4PF_6 for this reaction results in the precipitation of the orange complex [$(C_5Me_5)Rh(PPh_3)(dppe\text{-}P)$-$Cl]BPh_4$ after 5 minutes stirring at room temperature.

[$(C_5Me_5)Rh(dppm\text{-}P,P)Cl]Cl$ (176). Mixing [$(C_5Me_5)RhCl_2]_2$ (57 mg, 0.09 mmol) and dppm (71 mg, 0.18 mmol) in $CDCl_3$ (2 ml) at room temperature generates the complex [$(C_5Me_5)Rh(dppm\text{-}P)Cl_2$] (175), identified by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (see text). Over a period of 4 hours in solution the complex (175) rearranges to give the chelate complex (176) which may be recovered as a bright yellow solid on addition of toluene to the reaction solution. Yield 114 mg, 91%. Found C, 59.4; H, 5.4; Calc. for $C_{35}H_{35}P_2Cl_2Rh$ C, 61.5; H, 5.4.

[Pt($S_2CN^iPr_2$)(Ph_2PS)($PPhMe_2$)] (178). Prepared by stirring [$NH_2{}^iPr_2$][Pt($S_2CN^iPr_2$)(Ph_2PS)$_2$] (60 mg, 0.066 mmol) and $PPhMe_2$ (∿10 mg, 0.07 mmol) in chloroform (10 ml) at room temperature for 45 minutes. On reducing the volume of the reaction solution, addition of Et_2O precipitated the product as a pale yellow solid. Yield 29 mg, 61%. Found C, 45.4; H, 5.0; N, 2.1; Calc. for $C_{27}H_{35}NS_3P_2Pt$, C, 44.6; H, 4.8; N, 1.9. KBr disc i.r. spectrum ν_{CN} 1490, ν_{PS} 603 cm^{-1}. Prepared by the same method were [Pt($S_2CN^iPr_2$)(Ph_2PS)($PPhEt_2$)] (179). Using (6; ^{i}Pr) and $PPhEt_2$. Yield 52%. KBr disc i.r. spectrum ν_{CN} 1491, ν_{PS} 601 cm^{-1}.

[Pt(S_2CNEt_2)(Ph_2PS)($PPhMe_2$)] (180). Using equimolar quantities of [Pt(S_2CNEt_2)(Ph_2PO)(Ph_2PS)H] (7) and $PPhMe_2$. Yield 53%. KBr disc i.r. spectrum ν_{CN} 1518, ν_{PS} 605 cm^{-1}.

[Pt(S_2CNEt_2)(Ph_2PS)(PPh_3)] (181). Using [Pt(S_2CNEt_2)-(Ph_2PS)]$_2$ (8) and two equivalents of PPh_3. Yield 73%. M.p. 205°C. Found C, 49.6; H, 4.2; N, 1.18; Calc. for $C_{35}H_{35}NS_3P_2Pt$ C, 51.1; H, 4.3; N, 1.7. KBr disc i.r. spectrum ν_{CN} 1519, ν_{PS} 604 cm^{-1}. [(C_5Me_5)Rh(S_2CNEt_2)-(μ-dppe)Pt(Ph_2PS)($S_2CN^iPr_2$)]BPh_4 (182). Prepared by mixing [(C_5Me_5)Rh(S_2CNEt_2)(dppe-P)]BPh_4 (109) (31 mg, 0.028 mmol) and [$NH_2{}^iPr_2$][Pt($S_2CN^iPr_2$)(Ph_2PS)$_2$] (6; ^{i}Pr) (26 mg, 0.28 mmol) in $CDCl_3$ (2 ml) at room temperature. Addition of Et_2O to the reaction solution precipitated the product as a bright orange solid. Yield 34 mg, 72%. M.p. 124°C. Found C, 61.5; H, 5.7; N, 1.8; Calc. for $C_{84}H_{93}N_2P_3S_5BRhPt$ C, 59.6; H, 5.5; N, 1.7. KBr disc i.r. spectrum ν_{CN} 1502, 1512; ν_{PS} 610 cm^{-1}; *in situ* $^{31}P-\{^1H\}$ n.m.r. data of reaction

solution: refer to text. [(p-cym)Ru($PPhEt_2$)Cl(μ-dppe)-Pt(Ph_2PS)($S_2CN^iPr_2$)]BPh_4 (183). Generated by mixing [(p-cym)Ru($PPhEt_2$)(dppe-P)Cl]BPh_4 (137) (35 mg, 0.03 mmol) and (6; ^iPr) (27 mg, 0.03 mmol) in $CDCl_3$ (2 ml) at room temperature and characterised in situ by $^{31}P-\{^1H\}$ n.m.r. spectroscopy: refer to text.

TABLE 17: PHOSPHORUS-31-{^{1}H} NMR DATA FOR COMPLEXES PREPARED IN CHAPTER 5

COMPLEX [a,b]	δP_m	δP_x	δP_A	$J_{P_mP_x}$	$^2J_{P_AP_m}$	$J_{P_AP_x}$
$[(C_6H_6)Ru(PPhEt_2)(dppe\text{-}P)Cl]PF_6$ (136)[c]	29.3	-12.3	22.6	31.5	55.0	1.0
$[(p\text{-}cym)Ru(PPhEt_2)(dppe\text{-}P)Cl]BPh_4$ (137)[c]	27.0	-11.2	20.2	31.3	50.5	
$[(C_6H_6)Ru(PPhMe_2)(dppe\text{-}p)Cl]PF_6$ (138)[c]	29.3	-12.3	4.6	33.2	57.4	
$[(p\text{-}cym)Ru(PPhMe_2)(dppe\text{-}P)Cl]PF_6$ (139)[c]	27.7	-11.9	3.6	31.5	53.5	
$[(C_6H_6)Ru(PPh_3)(dppe\text{-}P)Cl]BPh_4$ (140)[c]	23.8	-12.1	25.2	32.5	54.9	
$[(p\text{-}cym)Ru(P(OMe)_3)(dppe\text{-}P)Cl]BPh_4$ (141)[c]	33.0	-12.1	119.8	35.3	80.9	
$[(C_6H_6)Ru(PPhMe_2)(dppm\text{-}P)Cl]PF_6$ (142)[c]	29.5	-23.8	4.3	43.5	58.1	2.0
$[(p\text{-}cym)Ru(PPhMe_2)(dppm\text{-}P)Cl]BPh_4$ (143)[c]	29.4	-26.3	2.3	41.2	54.5	
$[(p\text{-}cym)Ru(P(OMe)_3)(dppm\text{-}P)Cl]BPh_4$ (144)[c]	32.9	-27.8	120.2	40.3	80.6	
$[(C_6H_6)Ru(PPhMe_2)(dppp\text{-}P)Cl]PF_6$ (145)[c]	25.8	-17.9	5.0	1.4	57.6	
$[(p\text{-}cym)Ru(PPhMe_2)Cl(\mu\text{-}dppm)RuCl_2(p\text{-}cym)]BPh_4$ (150)[c,d]	22.0	25.2	4.0	52.0	53.5	
$[(p\text{-}cym)Ru(PPhEt_2)Cl(\mu\text{-}dppe)OsCl_2(p\text{-}cym)]BPh_4$ (151)[c]	22.8	-17.0	18.7	27.7	51.6	2.0
$[(C_6H_6)Ru(PPhMe_2)Cl(\mu\text{-}dppm)IrCl(COD)]PF_6$ (152)[c]	26.5	15.4	4.6	42.0	55.7	1.0
$[(p\text{-}cym)Ru(PPhEt_2)Cl(\mu\text{-}dppe)IrCl(COD)]BPh_4$ (153)[c]	24.6	16.6	19.6	32.1	50.3	0.7

TABLE 17 continued

COMPLEX	δP_B	δP_A	J_{12}	J_{34}	J_{56}
$\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppe})\}[PF_6]_2$ (146)[e]	30.9	5.8	19.6	59.2	0.6
$\{[(p\text{-cym})RuCl(PPhMe_2)]_2(\mu\text{-dppe})\}[PF_6]_2$ (147)[e]	27.6	2.9	19.0	55.1	1.4
$\{[(p\text{-cym})OsCl(PPhMe_2)]_2(\mu\text{-dppe})\}[PF_6]_2$ (148)[e]	-16.5	-44.0	19.5	35.4	3.0
$\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppp})\}[PF_6]_2$ (149)[f]	24.6	4.7		57.4	
$[(C_5Me_5)RhCl_2(dppe\text{-}P)]$ (174)[g]	30.8	-12.4	37.8	142.8	
$[(C_5Me_5)RhCl_2(dppm\text{-}P)]$ (175)[g]	30.8	-25.8	28.1	141.0	4.3
$[Pt(S_2CN^iPr_2)(Ph_2PS)(PPhMe_2)]$ (178)[h]	28.3	-14.2	3129.9	3437.5	24.4
$[Pt(S_2CN^iPr_2)(Ph_2PS)(PPhEt_2)]$ (179)[h]	26.6	6.3	3154.3	3435.1	24.3
$[Pt(S_2CNEt_2)(Ph_2PS)(PPhMe_2)]$ (180)[h]	28.2	-14.0	3165.9	3518.0	23.5
$[Pt(S_2CNEt_2)(Ph_2PS)(PPh_3)]$ (181)[h]	27.3	16.1	3106.4	3719.7	21.5
$[Pt(S_2CNEt_2)(Ph_2PS)(PEt_3)]$ (182)[h]	25.7	6.0	3206.1	3454.7	23.4

TABLE 17 continued

COMPLEX	δP_B	δP_A	J_{12}
[(p-cym)Ru(dppm-P)Cl_2] (155)[i]	25.7	-27.7	33.0
[(p-cym)Os(dppm-P)Cl_2] (156)[i]	-16.4	-28.6	34.8
[(p-cym)Ru(dppe-P)Cl_2] (157)[i]	25.5	-12.5	34.2
[(C_6H_6)Ru(dppe-P)Cl_2] (158)[i]	33.1	-12.5	39.0
[(p-cym)Ru(dppp-P)Cl_2] (159)[i]	23.7	-16.8	n/m
{[(p-cym)$RuCl_2$]$_2$(μ-dppm)} (160)	20.8		
{[(p-cym)$OsCl_2$]$_2$(μ-dppm)} (161)	-23.6		
{[(p-cym)$RuCl_2$]$_2$(μ-dppe)} (162)	24.0		
{[(C_6H_6)$RuCl_2$]$_2$(μ-dppe)} (163)	21.0		
{[(p-cym)$RuCl_2$]$_2$(μ-dppp)} (164)	22.5		
[(p-cym)$RuCl_2$(μ-dppm)$OsCl_2$(p-cym)] (165)[j]	19.4	-20.5	48.4
[(C_6H_6)Ru(dppe-P,P)Cl]Cl (168)	71.0		
[(C_6Me_6)Ru(dppm-P,P)Cl]PF_6 (169)	2.2		
[(C_6Me_6)Ru(dppe-P,P)Cl]PF_6 (170)	68.4		
[(C_6Me_6)Ru(dppp-P,P)Cl]PF_6 (171)	23.5		
[(p-cym)Ru(dppm-P,P)Cl]PF_6 (172)	1.7		
[(p-cym)Ru(dppe-P,P)Cl]BPh_4 (173)	71.2		
[(C_5Me_5)Rh(dppm-P,P)Cl]Cl (176)[k]	-4.8		114.1
[(C_5Me_5)Rh(dppe-P,P)Cl]PF_6 (177)[k]	64.0		131.8

NOTES FOR TABLE 17

a) Spectra obtained at 298°K in $CDCl_3$ unless otherwise stated.

b) δP/ppm; J/Hz

c) For definition of A,M and X subscripts refer to (136-145), (150) and (151) in text.

d) Spectrum obtained at 298°K in CD_2Cl_2.

e) Spectrum obtained at 298°K in CD_3NO_2. AA'BB' type spectrum. $P_A(PPhMe_2)$, P_B(dppe) $J_{12}=J_{P_BP_B'}$, $J_{34}=J_{P_AP_B}$ or $J_{P_A,P_B'}$, $J_{56}=J_{P_AP_B}$, or J_{P_A,P_B}.

f) Spectrum obtained at 298°K in CD_2Cl_2. AB type spectrum. P_A, P_B, J_{34} as above.

g) P_B(Rh bound P), P_A(uncood.P), $J_{12}=J_{PP}$, $J_{34}={}^1J_{RhP}$, $J_{56}={}^3J_{RhP}$.

h) $P_B(Ph_2PS^-)$, $P_A(PR_3)$, $J_{12}={}^1J_{PtP_B}$, $J_{34}={}^1J_{PtP_A}$, $J_{56}={}^2J_{P_AP_B}$.

i) P_B(M bound P), P_A(uncood.P), $J_{12}=J_{PP}$.

j) P_B(Ru bound P), P_A(Os bound P) $J_{12}={}^2J_{PP}$.

k) $J_{12}={}^1J_{RhP}$.

Table 18: Selected Bond Distances and Angles for the Dication $\{[(C_6H_6)RuCl(PPhMe_2)]_2(\mu\text{-dppe})\}^{2+}$ (146) with Estimated Standard Deviations in parenthesis

a) Distances (Å)

Ru - Cl	2.3980(25)	Ru - C(1)	2.261(6)
Ru - P(1)	2.3506(21)	Ru - C(2)	2.238(6)
Ru - P(2)	2.341(3)	Ru - C(3)	2.224(6)
P(2)-C(8)	1.841(12)	Ru - C(4)	2.233(6)
P(2)-C(9)	1.788(12)	Ru - C(5)	2.257(6)
P(2)-C(10)	1.828(6)	Ru - C(6)	2.271(6)
P(1)-C(7)	1.836(8)	C(7)-C(7')	1.555(16)

b) Angles (Degrees)

Cl - Ru - P(1)	88.38(8)	Ru - P(2) - C(8)	113.7(4)
Cl - Ru - P(2)	88.76(9)	Ru - P(2) - C(9)	121.1(4)
P(1)-Ru - P(2)	92.27(8)	Ru - P(2) - C(10)	111.12(22)
Ru - P(1)-C(7)	116.4(3)	P(1)-C(7) - C(7')	114.5(5)

APPENDIX 1

$^{31}P-\{^{1}H\}$ n.m.r. data for the Platinum-ligands used in Chapters 3 and 4. δP/ppm J_{xy}/Hz

COMPLEX	δP_s/se	$^{1}J_{PtPs}$/se	δP_B	$^{1}J_{PtP_B}$	$^{2}J_{PP}$	Other
$[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ (2)	61.4	3510.7				
$[Pt(S_2CN^{i}Pr_2)(Ph_2PO)_2H]$	61.8	3463.8				
$NH_2Et_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ (6)	27.1	3427.7				
$NH_2{}^{i}Pr_2[Pt(S_2CN^{i}Pr_2)(Ph_2PS)_2]$	28.2	3415.5				
$[Pt(S_2CNEt_2)(Ph_2PS)(Ph_2PO)H]$ (7)	30.5	3173.8	65.5	3774.4	26.9	
$[Pt(S_2CN^{i}Pr_2)(Ph_2PS)(Ph_2PO)H]$	31.8	3132.3	66.4	3723.2	26.9	
$[Pt(S_2CNEt_2)(Ph_2PS)]_2$ (8)	30.5	3656.4			13.6	$^{2}J_{PPt}$ 80.5
$[Pt(S_2CNEt_2)(Ph_2PS)(Ph_2POMe)]$ (9)	27.4	3085.9	91.7	4240.7	24.4	
$[Pt(S_2CN^{i}Pr_2)(Ph_2PS)(Ph_2POMe)]$	28.2	3056.6	92.7	4169.9	24.4	
$[Pt(S_2CNEt_2)(Ph_2PS)(Ph_2PH)]$ (10)	27.4	2996.5	5.1	3627.9	24.4	
$[Pt(S_2CN^{i}Pr_2)(Ph_2PS)(Ph_2PH)]$	29.3	2895.5	5.6	3559.6	24.4	
$[Pt(S_2CNEt_2)(Ph_2PSe)(Ph_2PH)]$ (5)	13.1	2902.8	7.8	3594.9	22.0	$^{1}J_{PSe}$ 399.0
$[Pt(S_2CN^{i}Pr_2)(Ph_2PSe)(Ph_2PH)]$	13.9	2869.1	8.5	3544.8	22.8	$^{1}J_{PSe}$ 371.3

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POSTGRADUATE COURSES AND CONFERENCES ATTENDED

'Aspects of Structural Chemistry'	Dr. C. Glidewell
'Organometallic Chemistry'	Dr. M. Schroder
'Molecular Electronics'	Prof.R.W. Munn Prof.J.O.Williams
'Recent Developments in Electrochemistry'	Dr.H.H.J.Girault Dr. G.A. Heath
'NMR Spectroscopy'	Dr. I.H. Saldler
'Modern Inorganic Chemistry' (3 lectures)	Prof. E.A.V.Ebsworth

Departmental and Research Seminars and Colloquia.

University of Strathclyde Inorganic Club Conferences 1984-86.

Second International Conference on the Chemistry of the Platinum Group Metals, 1-6th July 1984, Edinburgh, Scotland.

XXIV International Conference on Coordination Chemistry 24-29th August 1986, Athens, Greece.

Journal of Organometallic Chemistry, 284 (1985) C12—C14
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS AND REACTIONS OF SOME HETEROBIMETALLIC AND MULTIMETALLIC COMPLEXES CONTAINING η-ARENE-RUTHENIUM(II), -OSMIUM(II) AND η-PENTAMETHYLCYCLOPENTADIENYL-RHODIUM(III) MOIETIES

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(Received November 23rd, 1984)

Summary

Heterobimetallic complexes such as $[\eta\text{-areneMCl(SPPh}_2)_2\text{Pt(S}_2\text{CNEt}_2)]$ (I, M = Ru, Os) and $[\eta\text{-C}_5\text{Me}_5\text{RhCl(SPPh}_2)_2\text{Pt(S}_2\text{CNEt}_2)]$ (II) have been synthesised by reaction of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ with either $[M(\eta\text{-arene})Cl_2]_2$ or $[Rh(\eta\text{-C}_5Me_5)Cl_2]_2$ (2/1) molar ratio). Further reactions of I include facile chloride displacement with a range of neutral ligands L to give $[\eta\text{-areneML(SPPh}_2)_2\text{Pt(S}_2\text{CNEt}_2)]^+$ (III) cations and formation of tri- and penta-metallic species on treatment with more $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$.

In the last decade, extensive studies on the synthesis and reactivity of the binuclear complexes $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, p-$MeC_6H_4CHMe_2$, C_6Me_6 etc.) have been published [1]. Such studies include bridge cleavage reactions with a variety of Lewis bases L to give $[Ru(\eta\text{-arene})Cl_2L]$ or $[Ru(\eta\text{-arene})ClL_2]^+$ and with anionic ligands such as $^-S_2PR_2$, ^-O_2CR [2] (L—L) to afford either $[Ru(\eta\text{-arene})Cl(L—L)]$ or $[Ru(\eta\text{-arene})(L—L)_2]$. A wide range of homo-binuclear triple bridged cations of type $[Ru_2X_3(\eta\text{-arene})_2]^+$ (X = Cl, Br, I, OH, OR, SR), [3] $[Ru_2HXY(\eta\text{-arene})_2]^+$ (X = Y = Cl, OCOMe, $OCOCF_3$; X = Cl, Y = OCOMe or $OCOCF_3$) [4] and homo-tetranuclear cations such as $[Ru(\eta\text{-}C_6H_6)(OH)]_4^{4+}$ [5] and $[Ru_4(\eta\text{-}C_6H_6)_4(\mu_2\text{-OH})_4(\mu_4\text{-O}]^{2+}$ [6] are also available.

In this communication we report the high yield synthesis and some reactions of novel hetero-bimetallic and multimetallic compounds containing the $(\eta\text{-arene})Ru^{II}$ moiety and related complexes incorporating $(\eta$ arene$)Os^{II}$ and $(\eta\text{-}C_5Me_5)Rh^{III}$ fragments.

Thus, reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ with $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ [7] (1/2 molar ratio) in chloroform at ambient temperature gives,

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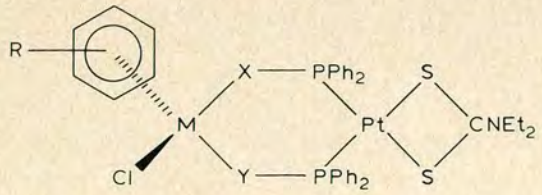
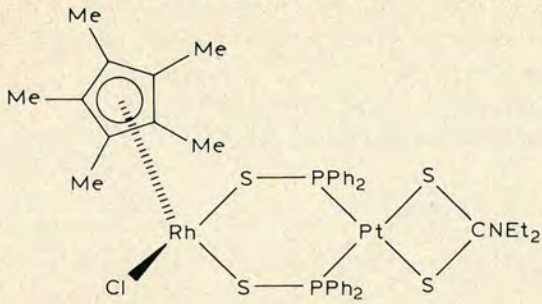


(Ia: M = Ru, X = Y = S;
Ib: M = Os, X = Y = S;
Ic: M = Ru, X = Y = O;
Id: M = Ru, X = O; Y = S)

on addition of methanol, high yields (75%) of the red solids [(η-arene)-$RuCl(SPPh_2)_2Pt(S_2CNEt_2)$] (Ia) (arene = C_6H_6, p-$MeC_6H_4CHMe_2$). The same products are formed by treatment of [$Ru(\eta$-arene)Cl(OCOMe)] with an equimolar amount of the $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ anion. Similarly, reaction of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ with either $[Os(p\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ or $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ (in 2/1 molar ratio) gives high yields of the corresponding yellow [η-p-$MeC_6H_4CHMe_2$)$OsCl(SPPh_2)_2Pt(S_2CNEt_2)$] (Ib) and dark red [$(\eta\text{-}C_5Me_5)RhCl(SPPh_2)_2Pt(S_2CNEt_2)$] (II) respectively*.



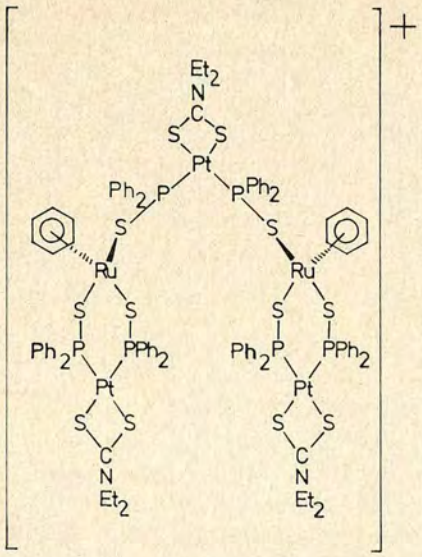
(II)

Likewise, preliminary studies indicate that treatment of $[Ru(\eta\text{-arene})Cl_2]_2$ with the anions $[Pt(S_2CNEt_2)(Ph_2PO)_2]^-$ and $[Pt(S_2CNEt_2)(Ph_2PO)Ph_2PS]^-$ [7] (in 1/2 molar ratio) yield the bimetallic complexes Ic and Id respectively.

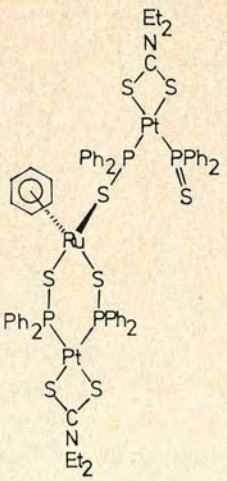
Reaction of Ia or Ib with neutral ligands (L) under relatively mild conditions, followed by addition of methanolic solutions of $Na[BPh_4]$ precipitates the heterobimetallic cations $[(arene)ML(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (III) (L = PPh_3, $PEtPh_2$, CO, PhC≡CH etc.). These cations can also be prepared in some instances by reaction of the monomers [$M(\eta$ arene)Cl_2L] with equimolar amounts of $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$*.

If Ia (arene = C_6H_6) is treated in chloroform with more $[Pt(S_2CNEt_2)$-$(Ph_2PS)_2]^-$ (2/1 molar ratio), the novel pentametallic cation IV is produced, whereas with equimolar ratios of Ia and the platinum anion, spectroscopic

*All these complexes have been fully characterised by elemental analyses, IR and ^1H, ^{31}P-$\{^1H\}$ and ^{13}C-$\{^1H\}$ NMR spectroscopy.



(IV)



(V)

evidence indicates the in situ formation of the trimetallic compound V containing bidentate and unidentate $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ groups.

Further studies on the stoichiometric and catalytic reactions of these compounds, including attempts to synthesise even more exotic multimetallic species starting from compounds of type V, e.g. $[(Et_2NCS_2)Pt(Ph_2PS)_2$-(arene)Ru-μ-{$SPPh_2Pt(S_2CNEt_2)PPh_2S$} $Os(arene)(SPPh_2)_2Pt(S_2CNEt_2]^+$ etc. are now in progress.

Acknowledgement. We thank Johnson—Matthey plc for loans of ruthenium trichloride, osmium tetroxide and rhodium trichloride and the SERC (JDF) for financial support.

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